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71 Applicant : **THE LUBRIZOL CORPORATION**
29400 Lakeland Boulevard
Wickliffe, Ohio 44092-2298 (US)

72 Inventor : **Schnur, Eric R.**
7695 Snowberry Court
Mentor, Ohio 44060 (US)
Inventor : **Richardson, Robert C.**
6348 Cumberland Drive
Mentor, Ohio 44060 (US)
Inventor : **Schwind, James J.**
Charnwood,
Church Lane,
Doveridge DE6 5NN, Derbyshire (GB)

74 Representative : **Crisp, David Norman et al**
D. YOUNG & CO.
21 New Fetter Lane
London EC4A 1DA (GB)

54 **Lubricating compositions with improved oxidation resistance containing a dispersant and an antioxidant.**

57 This invention relates to a lubricating composition comprising a major amount of an oil of lubricating viscosity with an iodine number less than about 9, (A) one or more antioxidant, and (B) from about 0.01% to about 3% by weight of at least one dispersant or detergent, wherein the total amount of antioxidant is at least about 2% by weight. The additives are useful act controlling oxidation of lubricants. Further, these lubricants have reduced viscosity increase caused by oxidation, while maintaining favorable carbon/varnish ratings.

This invention relates to a lubricating composition having improved oxidation inhibition properties.

Lubricating compositions serve to remove heat from operating equipment. These compositions also act to reduce metal-metal contact which lead to wearing. Today many pieces of equipment are reduced in size, which in turn has lead to higher operating temperatures for the equipment. These higher temperatures may lead to increased oxidation of the lubricating composition.

Today the drain intervals for lubricants have increased. When a lubricant has to operate for longer periods at higher temperatures, the lubricant is prone to viscosity increase. The viscosity increase is believed to be caused by polymerization of oxidized components of the lubricants. This increased viscosity renders the lubricant unfit for use. It is desirable to have lubricants with improved oxidation resistance. More particularly, it is desirable to have lubricants which will withstand long periods of operation at high temperatures.

This invention relates to a lubricating composition comprising a major amount of an oil of lubricating viscosity with an iodine number less than about 9, (A) one or more antioxidant, and (B) from about 0.01% to about 3 % by weight of at least one dispersant or detergent, wherein the total amount of antioxidant is at least about 2% by weight. The additives are useful act controlling oxidation of lubricants. Further, these lubricants have reduced viscosity increase caused by oxidation, while maintaining favorable carbon/varnish ratings.

Various preferred features and embodiments of the invention will now be described by way of non-limiting invention.

The term "hydrocarbyl" includes hydrocarbon as well as substantially hydrocarbon groups. Substantially hydrocarbon describes groups which contain heteroatom substituents that do not alter the predominantly hydrocarbon nature of the substituent. Examples of hydrocarbyl groups include the following:

(1) hydrocarbon substituents, i.e., aliphatic (e.g., alkyl or alkenyl) and alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic substituents and the like as well as cyclic substituents wherein the ring is completed through another portion of the molecule (that is, for example, any two indicated substituents may together form an alicyclic radical);

(2) substituted hydrocarbon substituents, i.e., those substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; those skilled in the art will be aware of such groups (e.g., halo (especially chloro and fluoro), hydroxy, mercapto, nitro, nitroso, sulfoxy, etc.);

(3) heteroatom substituents, i.e., substituents which will, while having a predominantly hydrocarbon character within the context of this invention, contain an atom other than carbon present in a ring or chain otherwise composed of carbon atoms (e.g., alkoxy or alkylthio). Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as, e.g. parietal, furyl, thienyl, imidazolyl, etc.

In general, no more than about 2, preferably no more than one heteroatom substituent will be present for every ten carbon atoms in the hydrocarbyl group. Typically, there will be no such heteroatom substituents in the hydrocarbyl group. Therefore, the hydrocarbyl group is purely hydrocarbon.

As described above, the lubricating composition contains an oil of lubricating viscosity which has an iodine value of less than about 9. Iodine value is determined according to ASTM-D-460. In one embodiment, the oil of lubricating viscosity has a iodine value less than about 8, or less than about 6, or less than about 4. The oil of lubricating viscosity includes natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, mineral lubricating oils, and solvent or acid treated mineral oils. Synthetic lubricating oils include hydrocarbon oils (polyalpha-olefins), halo-substituted hydrocarbon oils, alkylene oxide polymers, esters of dicarboxylic acids and polyols, esters of phosphorus-containing acids, polymeric tetrahydrofurans and silicon-based oils. Preferably, the oil of lubricating viscosity is a hydrotreated mineral oil or a synthetic lubricating oil, such a polyolefin. Examples of useful oils of lubricating viscosity include XHVI basestocks, such as 100N isomerized wax basestock (0.01 % sulfur/ 141 VI), 120N isomerized wax basestock (0.01 % sulfur/ 149 VI), 170N isomerized wax basestock (0.01 % sulfur/ 142 VI), and 250N isomerized wax basestock (0.01% sulfur/ 146 VI); refined basestocks, such as 250N solvent refined paraffinic mineral oil (0.16% sulfur/89 VI), 200N solvent refined naphthenic mineral oil (0.2% sulfur/ 60 VI), 100N solvent refined/ hydrotreated paraffinic mineral oil (0.01% sulfur/98 VI), 240N solvent refined/ hydrotreated paraffinic mineral oil (0.01 % sulfur/ 98 VI), 80N solvent refined/ hydrotreated paraffinic mineral oil (0.08% sulfur/ 127 VI), and 150N solvent refined/ hydrotreated paraffinic mineral oil (0.17% sulfur/ 127 VI). A description of oils of lubricating viscosity occurs in U.S. Patent 4,582,618 (column 2, line 37 through column 3, line 63, inclusive), herein incorporated by reference for its disclosure to oils of lubricating viscosity.

In one embodiment, the oil of lubricating viscosity is a polyalpha-olefin (PAO). Typically, the polyalpha-olefins are derived from monomers having from about 4 to about 30, or from about 4 to about 20, or from about 6 to about 16 carbon atoms. Examples of useful PAOs include those derived from decene. These PAOs may have a viscosity from about 3 to about 150, or from about 4 to about 100, or from about 4 to about 8 cSt at

100°C. Examples of PAOs include 4 cSt polyolefins, 6 cSt polyolefins, 40 cSt polyolefins and 100 cSt polyalphaolefins.

Table 1 contains examples of oils of lubricating viscosity. The iodine value for the oils and oil mixtures is determined by ASTM D-460.

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TABLE I

| | I | II | III | IV | V | VI | VII | VIII | IX | X | XI | XII |
|---|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|
| HVI 250N solvent refined paraffinic mineral oil | | | | 10 | 50 | 100 | | | | | | |
| MVI 200N solvent refined naphthenic mineral oil | | 10 | 50 | | | | | | | | | |
| XHVI 100N isomerized wax basestock | | | | | | | | | | 90 | | |
| XHVI 120N isomerized wax basestock | 100 | 90 | 50 | 90 | 50 | | | | | | | |
| XHVI 250N isomerized wax basestock | | | | | | | | | | 10 | | |
| 170N isomerized wax basestock | | | | | | | 100 | | | | | |
| A 6 cSt PAO | | | | | | | | 100 | | | | |
| A 4 cSt PAO | | | | | | | | | 100 | | | |
| 100N solvent refined/ hydrotreated paraffinic mineral oil | | | | | | | | | | | 80 | |
| 240N solvent refined/ hydrotreated paraffinic mineral oil | | | | | | | | | | | 20 | |
| 80N solvent refined/ hydrotreated paraffinic mineral oil | | | | | | | | | | | | 70 |
| 150N solvent refined/ hydrotreated paraffinic mineral oil | | | | | | | | | | | | 30 |
| Iodine Value (ASTM D-460) | 0.4 | 1.5 | 6.1 | 1.2 | 4.4 | 8.5 | 0.6 | 0.5 | 0.4 | 1.3 | 0.5 | 3.2 |

In one embodiment, the oil of lubricating viscosity are selected to provide lubricating compositions with a

kinematic viscosity of at least about 3.5 cSt, or at least about 4.0 cSt at 100°C. In one embodiment, the lubricating compositions have an SAE gear viscosity number of at least about SAE 70W, or at least about SAE 75W. The lubricating composition may also have a so-called multigrade rating such as SAE 75W-80, 75W-90, 75W-90, 75W-140, 80W-90, or 80W-140. Multigrade lubricants may include a viscosity improver which is formulated with the oil of lubricating viscosity to provide the above lubricant grades. Useful viscosity improvers include but are not limited to polyolefins, such as ethylene-propylene copolymers, or polybutylene rubbers, including hydrogenated rubbers, such as styrene-butadiene or styrene-isoprene rubbers; or polyacrylates, including polymethacrylates. In one embodiment, the viscosity improver is a polyolefin or polymethacrylate. Viscosity improvers available commercially include Acryloid™ viscosity improvers available from Rohm & Haas; Shellvis™ rubbers available from Shell Chemical; Trilene™ polymers, such as Trilene™ CP-40, available commercially from Uniroyal Chemical Co., and Lubrizol 3100 series and 8400 series polymers, such as Lubrizol 3174 available from The Lubrizol Corporation.

In one embodiment, the oil of lubricating viscosity includes at least one ester of a dicarboxylic acid. Typically the esters containing from about 4 to about 30, preferably from about 6 to about 24, or from about 7 to about 18 carbon atoms in each ester group. Here, as well as elsewhere, in the specification and claims, the range and ratio limits may be combined. Examples of dicarboxylic acids include glutaric, adipic, pimelic, suberic, azelaic and sebacic. Example of ester groups include hexyl, octyl, decyl, and dodecyl ester groups. The ester groups include linear as well as branched ester groups such as iso arrangements of the ester group. A particularly useful ester of a dicarboxylic acid is diisodecyl azelate.

In another embodiment, the oil of lubricating viscosity is selected to provide lubricating compositions for crankcase applications, such as for gasoline and diesel engines. Typically, the lubricating compositions are selected to provide an SAE crankcase viscosity number of 10W, 20W, or 30W lubricants. The lubricating composition may also have a so called multi-grade rating such as SAE 5W-30, 10W-30, 10W-40, 20W-50, etc. As described above, multigrade lubricants include a viscosity improver which is formulated with the oil of lubricating viscosity to provide the above lubricant grades.

(A) Antioxidant

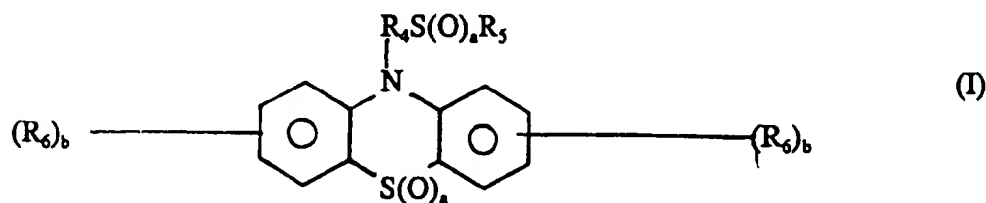
The lubricating compositions also include one or more antioxidants which are present in a total amount of at least about 2 % by weight. Generally, the antioxidants are present in an amount from about 2.2% up to about 10%, or from about 2.5% up to about 8%, or from about 3% up to about 7% by weight. The antioxidants include amine antioxidants, dithiophosphoric esters, phenol antioxidants, dithiocarbamates, aromatic phosphites, and sulfurized fatty oils and olefins. In one embodiment, the antioxidant (A) is a sulfur free antioxidant, preferably an amine antioxidant, or a dithiocarbamate, preferably an alkylene coupled dithiocarbamate.

Amine antioxidants include alkylated aromatic amines and heterocyclic amines. The alkylated aromatic amines include compounds represented by the formula $Ar^1-NR_1-Ar^2$, wherein Ar^1 and Ar^2 are independently mononuclear or polynuclear, substituted or unsubstituted aromatic groups; and R_1 is hydrogen, halogen, OH, NH_2 , SH, NO_2 or a hydrocarbyl group having from 1 to about 50 carbon atoms. The aromatic group as represented by "Ar", as well as elsewhere in other formulae in this specification and in the appended claims, may be mononuclear or polynuclear. Examples of mononuclear Ar moieties include benzene moieties, such as 1,2,4-benzenetriyl; 1,2,3-benzenetriyl; 3-methyl-1,2,4-benzenetriyl; 2-methyl-5-ethyl-1,3,4-benzenetriyl; 3-propoxy-1,2,4,5-benzenetetrail; 3-chloro-1,2,4-benzenetriyl; 1,2,3,5-benzenetetrail; 3-cyclohexyl-1,2,4-benzenetriyl; and 3-azocyclopentyl-1,2,5-benzenetriyl, and pyridine moieties, such as 3,4,5-azabenzene; and 6-methyl-3,4,5-azabenzene. The polynuclear groups may be those where an aromatic nucleus is fused at two points to another aromatic nucleus, such as naphthyl and anthracenyl groups. Specific examples of fused ring aromatic moieties Ar include: 1,4,8-naphthylene; 1,5,8-naphthylene; 3,6-dimethyl-4,5,8(1-azonaphthalene); 7-methyl-9-methoxy-1,2,5, 9-anthracenetetrail; 3,10-phenathrylene; and 9-methoxy-benz(a)phenanthrene-5,6,8,12-yl. The polynuclear group may be those where at least two nuclei (either mononuclear or polynuclear) are linked through bridging linkages. These bridging linkages may be chosen from the group consisting of alkylene linkages, ether linkages, keto linkages, sulfide linkages, and polysulfide linkages of 2 to about 6 sulfur atoms. Specific examples of Ar when it is linked polynuclear aromatic moiety include: 3,3',4,4',5-bibenzenetetrail; di(3,4-phenylene)ether; 2,3-phenylene-2,6-naphthylenemethane; and 3-methyl,9H-fluorene-1,2,4,5,8-yl; 2,2-di(3,4-phenylene)propane; sulfur-coupled 3-methyl-1,2,4-benzatriyl(having 1 to about 10 thiomethylphenylene groups); and amino-coupled 3-methyl-1,2,4-benzatriyl (having 1 to about 10 aminomethylphenylene groups). Typically Ar is a benzene nucleus, lower alkylene bridged benzene nucleus, or a naphthalene nucleus.

In another embodiment, the alkylated aromatic amine is represented by the formula $R_2-Ar-NH-Ar-R_3$, wherein R_2 and R_3 are independently hydrogen or hydrocarbyl groups having from 1 to about 50, or from about 4 to about 20 carbon atoms. Examples of aromatic amines include p,p'-dioctyldiphenylamine; octylphenyl-beta-

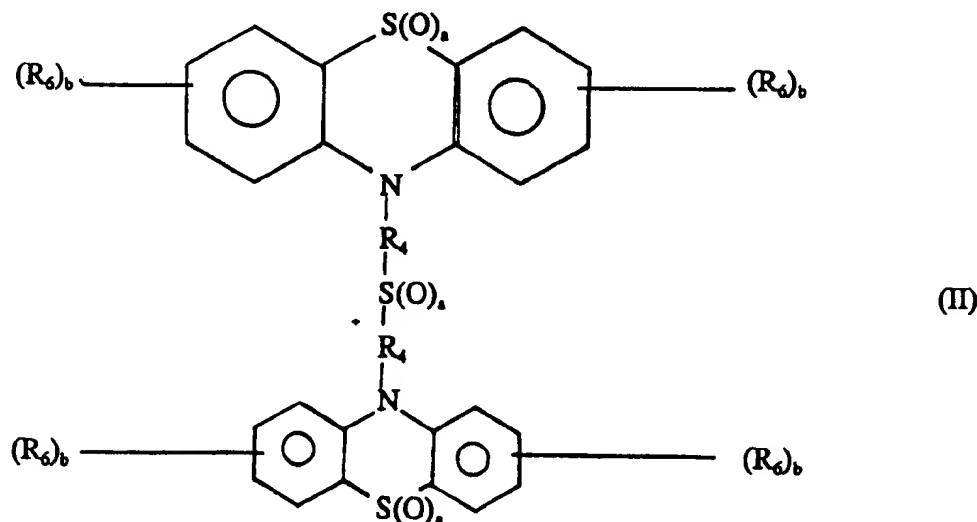
naphthylamine; octylphenyl-alpha-naphthylamine, phenyl-alpha-naphthylamine; phenyl-beta-naphthylamine; p-octylphenyl-alpha-naphthylamine and 4-octylphenyl-1-octyl-beta-naphthylamine and di(nonylphenyl)amine, with di(nonylphenyl)amine preferred. U.S. Patents 2,558,285; 3,601,632; 3,368,975; and 3,505,225 disclose diarylamines useful as antioxidant (A). These patents are incorporated herein by reference.

In another embodiment, the antioxidant (A) may be a phenothiazine. Phenothiazines include phenothiazine, substituted phenothiazine, or derivatives, such as those represented by the formula



wherein R_4 is an alkylene, alkenylene or an aralkylene group, or mixtures thereof, R_5 is selected from the group consisting of higher alkyl groups, or an alkenyl, aryl, alkaryl or aralkyl group and mixtures thereof; each R_6 is independently alkyl, alkenyl, aryl, alkaryl, arylalkyl, halogen, hydroxyl, alkoxy, alkylthio, arylthio, or fused aromatic rings, or mixtures thereof; a and b are each independently 0 or greater. In one embodiment, R_4 contains from about 2 to about 8, or two or three carbon atoms. R_5 typically contains from about 3 to about 30, or from about 4 to about 15 carbon atoms. R_6 contains from 1 to about 50, or from about 4 to about 30, or from 6 to about 20 carbon atoms.

In another embodiment, the phenothiazine derivatives may be represented by the formula



wherein R_4 , R_6 , a and b are as defined with respect to Formula I.

The above-described phenothiazine derivatives, and methods for their preparation are described in U.S. Patent 4,785,095, and the disclosure of this patent is hereby incorporated by reference for its teachings of such methods and compounds. In one embodiment, a dialkyldiphenylamine is treated with sulfur at an elevated temperature such as in the range of 145°C to 205°C for a sufficient time to complete the reaction. A catalyst such as iodine may be utilized to establish the sulfur bridge.

Phenothiazine and its various derivatives may be converted to the above compounds by contacting the phenothiazine compound containing the free NH group with a thioalcohol of the formula R_5SR_4OH where R_4 and R_5 are defined with respect to Formula I. The thioalcohol may be obtained by the reaction of a mercaptan, such as hexanethiol, octanethiol and dodecanethiol, with an alkylene oxide, such as ethylene or propylene oxide under basic conditions. Alternatively, the thioalcohol may be obtained by reacting a terminal olefin, such as those described herein, with mercaptoethanol under free radical conditions.

When it is desired to prepare compounds of the type represented by Formulae I and II wherein a is 1 or 2, i.e., sulfones or sulfoxides, the derivatives prepared by the reaction with the thioalcohols described above

are oxidized with an oxidizing agent, such as hydrogen peroxide, in a solvent such as glacial acetic acid or ethanol under an inert gas blanket. The partial oxidation takes place conveniently at from about 20°C to about 150°C. The following examples illustrate the preparation of phenothiazines.

In one embodiment, the antioxidant may be a phosphorus ester. The ester includes reaction products of a phosphorus acid with an unsaturated compound. The phosphorus acids include the phosphoric, phosphonic, phosphinic and thiophosphoric acids, including dithiophosphoric acid, as well as the monothiophosphoric acid, thiophosphinic and thiophosphonic acids. The phosphorus acid is typically prepared by reacting one or more phosphorus acid or anhydride with an alcohol containing from one to about 30, or from two to about 24, or from about 3 to about 12 carbon atoms. The phosphorus acid or anhydride is generally an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide, phosphorous acid, phosphoric acid, phosphorus halide, C₁₋₇ phosphorus esters, or a phosphorus sulfide which includes phosphorus pentasulfide, phosphorus sesquisulfide, phosphorus heptasulfide and the like. Alcohols used to prepare the phosphorus acid esters include butyl, amyl, 2-ethylhexyl, hexyl, octyl, oleyl, and cresol alcohols. Examples of commercially available alcohols include Alfol 810 (a mixture of primarily straight chain, primary alcohols having from 8 to 10 carbon atoms); Alfol 1218 (a mixture of synthetic, primary, straight-chain alcohols containing 12 to 18 carbon atoms); Alfol 20+ alcohols (mixtures of C₁₈-C₂₈ primary alcohols having mostly C₂₀ alcohols as determined by GLC (gas-liquid-chromatography)); and Alfol 22+ alcohols (C₁₈-C₂₈ primary alcohols containing primarily C₂₂ alcohols). Alfol alcohols are available from Continental Oil Company. Another example of a commercially available alcohol mixtures are Adol 60 (about 75 % by weight of a straight chain C₂₂ primary alcohol, about 15% of a C₂₀ primary alcohol and about 8% of C₁₈ and C₂₄ alcohols) and Adol 320 (oleyl alcohol). The Adol alcohols are marketed by Ashland Chemical.

A variety of mixtures of monohydric fatty alcohols derived from naturally occurring triglycerides and ranging in chain length of from C₈ to C₁₈ are available from Procter & Gamble Company. These mixtures contain various amounts of fatty alcohols containing mainly 12, 14, 16, or 18 carbon atoms. For example, CO-1214 is a fatty alcohol mixture containing 0.5% of C₁₀ alcohol, 66.0% of C₁₂ alcohol, 26.0% of C₁₄ alcohol and 6.5% of C₁₈ alcohol.

Another group of commercially available mixtures include the "Neodol" products available from Shell Chemical Co. For example, Neodol 23 is a mixture of C₁₂ and C₁₃ alcohols; Neodol 25 is a mixture of C₁₂ and C₁₅ alcohols; and Neodol 45 is a mixture of C₁₄ to C₁₅ linear alcohols. Neodol 91 is a mixture of C₉, C₁₀ and C₁₁ alcohols.

Fatty vicinal diols also are useful and these include those available from Ashland Oil under the general trade designation Adol 114 and Adol 158. The former is derived from a straight chain alpha-olefin fraction of C₁₁-C₁₄, and the latter is derived from a C₁₅-C₁₈ alphaolefin fraction.

In one embodiment, the phosphorus acid is a thiophosphorus acid or salt thereof. The thiophosphorus acid or salt may be prepared by reacting one or more phosphorus sulfides, such as those described above with alcohols, such as those described above. The thiophosphorus acid esters may be mono- or dithiophosphorus acid esters. Thiophosphorus acid esters are also referred to generally as dithiophosphates.

In one embodiment, the phosphorus acid is a monothiophosphoric acid. Monothiophosphoric acids may be prepared by the reaction of a sulfur source with a dihydrocarbyl phosphite. The sulfur source may for instance be elemental sulfur, or a sulfide, such as a sulfur coupled olefin or a sulfur coupled dithiophosphate. Elemental sulfur is a preferred sulfur source. The preparation of monothiophosphoric acids is disclosed in U.S. Patent 4,755,311 and PCT Publication WO 87/07638, which are incorporated herein by reference for their disclosure of monothiophosphoric acids, sulfur sources, and the process for making monothiophosphoric acids. Monothiophosphoric acids may also be formed in the lubricant blend by adding a dihydrocarbyl phosphite to a lubricating composition containing a sulfur source, such as a sulfurized olefin. The phosphite may react with the sulfur source under blending conditions (i.e., temperatures from about 30°C to about 100°C, or higher) to form the monothiophosphoric acid.

In another embodiment, the phosphorus acid is a dithiophosphoric acid or phosphorodithioic acid. The dithiophosphoric acid may be represented by the formula (R₇O)₂PSSH, wherein each R₇ is independently a hydrocarbyl group containing from about 3 to about 30, or from about 3 up to about 18, or from about 4 up to about 12, or up to about 8 carbon atoms. Examples of R₇ include isopropyl, isobutyl, n-butyl, sec-butyl, amyl, n-hexyl, methylisobutyl carbonyl, heptyl, 2-ethylhexyl, isooctyl, nonyl, behenyl, decyl, dodecyl, tridecyl, alkylphenyl groups, or mixtures thereof. Illustrative lower alkylphenyl R₇ groups include butylphenyl, amylphenyl, and heptylphenyl and mixtures thereof. Examples of mixtures of R₇ groups include: 1-butyl and 1-octyl; 1-pentyl and 2-ethyl-1-hexyl; isobutyl and n-hexyl; isobutyl and isoamyl; 2-propyl and 2-methyl-4-pentyl; isopropyl and sec-butyl; and isopropyl and isooctyl.

As described above, the phosphoric acids are reacted with an unsaturated compound to form the phos-

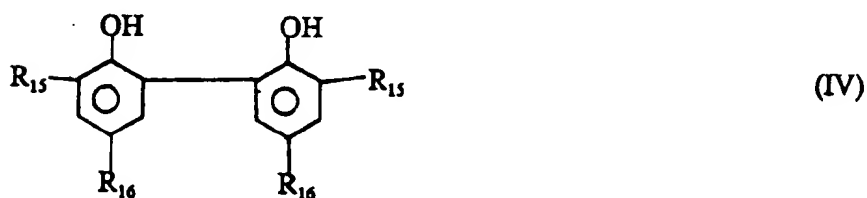
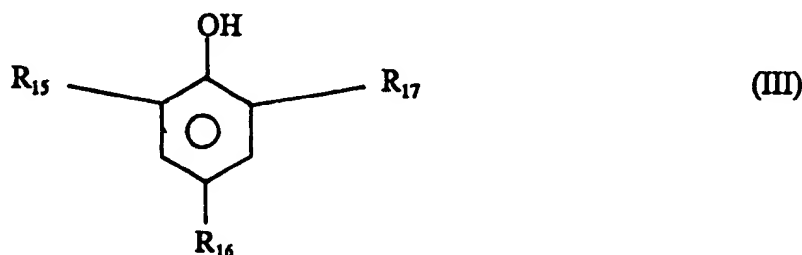
phorus esters. The unsaturated compounds include unsaturated amides, esters, acids, epoxides, and ethers. Examples of unsaturated amides include acrylamide, N,N'-methylene bis(acrylamide), methacrylamide, crotonamide, and the like. The reaction product of the phosphorus acid and the unsaturated amide may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. Examples of phosphorus containing amides include the reaction product of di(methylamyl) dithiophosphoric acid and acrylamide and the reaction product of di(amyl) dithiophosphoric acid, acrylamide and paraformaldehyde. The phosphorus containing amides are known in the art and are disclosed in U.S. Patents 4,670,169, 4,770,807, and 4,876,374 which are incorporated by reference for their disclosures of phosphorus amides and their preparation.

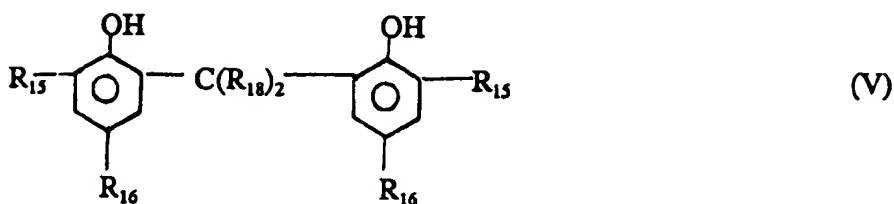
In another embodiment, the unsaturated compound is an unsaturated carboxylic acid or ester. Examples of unsaturated carboxylic acids and anhydrides include acrylic acid or esters, methacrylic acid or esters, itaconic acid or esters, fumaric acid or esters, and maleic acid, anhydride, or esters. The esters may be represented by one of the formulae $R_8C=C(R_9)C(O)OR_{10}$, or $R_{10}O-(O)C-HC=CH-C(O)OR_{10}$, wherein each R_8 and R_{10} are independently hydrogen or a hydrocarbyl group having from one to about eighteen, or from one to about twelve, or from one to about eight carbon atoms, R_9 is hydrogen or an alkyl group having from one to about six carbon atoms. In one embodiment, R_9 is preferably hydrogen or a methyl group. Examples of unsaturated carboxylic esters include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, ethyl maleate, butyl maleate and 2-ethylhexyl maleate. The above list includes mono- as well as diesters of maleic, fumaric and citraconic acids. If the carboxylic acid is used, the ester may then be formed by subsequent reaction of the phosphoric acid-unsaturated carboxylic acid adduct with an alcohol, such as those described above. Examples of phosphorus containing esters are the reaction product of isobutyl, amyl dithiophosphoric acid and methyl acrylate and di(amyl)dithiophosphoric acid and butyl methacrylate.

In another embodiment, the unsaturated compound is a vinyl ether. The vinyl ether is represented by the formula $R_{11}-CH_2=CH-OR_{12}$, wherein R_{11} and R_{12} are independently hydrogen or a hydrocarbyl group having from 1 up to about 30, or from 1 up to about 24, or from 2 up to about 12 carbon atoms. Examples of vinyl ethers include methyl vinyl ether, propyl vinyl ether, 2-ethylhexyl vinyl ether and the like.

In another embodiment, the unsaturated compound is a vinyl ester. The vinyl ester may be represented by the formula $R_{13}CH=CH-O(O)CR_{14}$, wherein R_{13} is a hydrocarbyl group having from 1 to about 30, or from 1 to about 12 carbon atoms, preferably hydrogen, and R_{14} is a hydrocarbyl group having 1 to about 30, or from 1 to about 12, or from 1 to about 8 carbon atoms. Examples of vinyl esters include vinyl acetate, vinyl 2-ethylhexanoate, vinyl butanoate, etc.

In another embodiment, the antioxidant (A) is at least one phenol antioxidant. The phenol antioxidants include metal and metal free hindered phenols. Alkylene coupled derivatives of hindered phenols and phenol sulfides or sulfur coupled phenols may also be used. Hindered phenols are defined as those containing a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds wherein the hydroxyl groups are in the o- or p-position to each other. The metal-free hindered phenols may be represented by the following formulae:





wherein each R_{15} is independently a hydrocarbyl group containing from 3 to about 9 carbon atoms, each R_{16} is hydrogen or a hydrocarbyl group, R_{17} is hydrogen or a hydrocarbyl group containing from 1 to about 9 carbon atoms, and each R_{18} is independently hydrogen or a methyl group. In one embodiment, R_{16} is an alkyl group containing from about 3 to about 50, or from about 6 to about 20, or from about 6 to about 12 carbon atoms. In one embodiment alkyl groups are derived from polymers of ethylene, propylene, 1-butene and isobutene, preferably propylene tetramer or trimer. Examples of such groups include hexyl, heptyl, octyl, decyl, dodecyl, tripropenyl, tetrapropenyl, etc. Examples of R_{15} , R_{16} and R_{17} groups include propyl, isopropyl, butyl, sec-butyl, tert-butyl, heptyl, octyl, and nonyl. In another embodiment, each R_{15} and R_{17} are tertiary groups, such as tert-butyl or tert-amyl groups. The phenolic compounds may be prepared by various techniques, and in one embodiment, such phenols are prepared in stepwise manner by first preparing the para-substituted alkylphenol, and thereafter alkylating the para-substituted phenol in the 2- and/or 6-position as desired. When it is desired to prepare coupled phenols of the type represented by Formulae IV and V, the second step alkylation is conducted under conditions which result in the alkylation of only one of the positions ortho to the hydroxyl group. Examples of useful phenolic materials include: 2-t-butyl-4-heptylphenol; 2-t-butyl-4-octylphenol; 2-t-butyl-4-dodecylphenol; 2,6-di-t-butyl-4-butylphenol; 2,6-di-t-butyl-4-heptylphenol; 2,6-di-t-butyl-4-dodecylphenol; 2,6-di-t-butyl-tetrapropenylphenol; 2-methyl-6-di-t-butyl-4-heptylphenol; 2,6-di-t-butyl-tripropenylphenol; 2,4-dimethyl-6-t-butylphenol; 2,6-t-butyl-4-ethylphenol; 4-t-butylcatechol; 2,4-di-t-butyl-p-cresol; 2,6-di-t-butyl-4-methylphenol; and 2-methyl-6-di-t-butyl-4-dodecylphenol. Examples of the ortho coupled phenols include: 2,2'-bis(6-t-butyl-4-heptylphenol); 2,2'-bis(6-t-butyl-4-octylphenol); 2,6-bis-(1'-methylcyclohexyl)-4-methylphenol; and 2,2'-bis(6-t-butyl-4-dodecylphenol).

Alkylene-coupled phenolic compounds may be prepared from the phenols by reaction of the phenolic compound with an aldehyde, typically those containing from one to about eight carbon atoms, such as formaldehyde or acetaldehyde, aldehyde precursors, such as paraformaldehyde or trioxane, or a ketone, such as acetone. The alkylene-coupled phenols may be obtained by reacting from 0.3 to about 2 moles a phenol with 1 equivalent of an aldehyde or ketone. Procedures for coupling of phenolic compounds with aldehydes and ketones are known to those in the art. Examples of phenolic compounds include 2,2'-methylenebis(6-t-butyl-4-heptylphenol); 2,2'-methylenebis(6-t-butyl-4-octylphenol); 2,2'-methylenebis(4-dodecyl-6-t-butylphenol); 2,2'-methylenebis(4-octyl-6-t-butylphenol); 2,2'-methylenebis(4-octylphenol); 2,2'-methylenebis(4-dodecylphenol); 2,2'-methylenebis(4-heptylphenol); 2,2'-methylenebis(6-t-butyl-4-dodecylphenol); 2,2'-methylenebis(6-t-butyl-4-tetrapropenylphenol); and 2,2'-methylenebis(6-t-butyl-4-butylphenol).

In another embodiment, the antioxidant (A) is a metal-free (or ashless) alkylphenol sulfide or sulfur coupled phenols. The alkylphenols from which the sulfides are prepared also may comprise phenols of the type discussed above and represented by Formula III wherein R_{17} is hydrogen. For example, the alkylphenols which can be converted to alkylphenol sulfides include: 2-t-butyl-4-heptylphenol; 2-t-butyl-4-octylphenol; and 2-t-butyl-4-dodecylphenol; 2-t-butyl-4-tetrapropenylphenol. The term "alkylphenol sulfides" is meant to include di-(alkylphenol) monosulfides, disulfides, and polysulfides, as well as other products obtained by the reaction of the alkylphenol with sulfur monochloride, sulfur dichloride or elemental sulfur. One mole of phenol typically is reacted with about 0.5-1.5 moles, or higher, of sulfur compound. For example, the alkylphenol sulfides are readily obtained by mixing, one mole of an alkylphenol and 0.5-2.0 moles of sulfur dichloride. The reaction mixture is usually maintained at about 100°C for about 2-5 hours, after which time the resulting sulfide is dried and filtered. When elemental sulfur is used, temperatures from about 150-250°C or higher are typically used. It is also desirable that the drying operation be conducted under nitrogen or a similar inert gas. A particularly useful alkylphenol sulfide is thio-bis(tetrapropenylphenate).

Suitable basic alkylphenol sulfides are disclosed, for example, in U.S. Patents 3,372,116; 3,410,798; and 4,021,419, which are hereby incorporated by reference. These sulfur-containing phenolic compositions described in U.S. Patent 4,021,419 are obtained by sulfurizing a substituted phenol with sulfur or a sulfur halide and thereafter reacting the sulfurized phenol with formaldehyde or an aldehyde precursor, e.g., paraformaldehyde or trioxane. Alternatively the substituted phenol may be first reacted with formaldehyde or paraformaldehyde and thereafter reacted with sulfur or a sulfur halide to produce the desired alkylphenol sulfide.

In another embodiment, the antioxidant (A) is a dithiocarbamate antioxidant. The dithiocarbamate antioxidants include reaction products of a dithiocarbamic acid or salt and one or more of the above described unsaturated compounds, such as unsaturated amides, carboxylic acids, anhydrides, or esters, or ethers; alkylene-coupled dithiocarbamates; and bis(S-alkyldithiocarbamoyl) disulfides. In one embodiment, the dithiocarbamate compounds are ashless, i.e. metal free. The dithiocarbamic acid or salts may be prepared by simultaneously reacting an amine, carbon disulfide and one or more of the above unsaturated compounds. Generally, the reaction occurs at a temperature from about 25°C, or from about 50°C to about 125°C, or to about 100°C. U. S. Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making the same. These patents are hereby incorporated by reference for their disclosure of dithiocarbamate compounds and method of making the same.

The dithiocarbamic acid or salt may be prepared by reacting an amine with carbon disulfide. The amine may be a primary or a secondary amine. The amine may be a mono- or polyamine, such as those described herein. The amines may be primary or secondary amines, with secondary amines preferred. The amines generally may contain hydrocarbyl groups independently having from 1 up to about 40, or from about 2 up to about 30, or from 3 up to about 24, or even up to about 12 carbon atoms. In one embodiment, the amines are primary amines. Examples of primary amines useful in the present invention include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine.

In one embodiment, the primary amine is a fatty amine, such as those containing from about 8 to about 30, or from about 12 to about 24 carbon atoms. The fatty amines include n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, oleyamine, etc. Also useful fatty amines include commercially available fatty amines such as "Armeen" amines (products available from Akzo Chemicals, Chicago, Illinois), such as Akzo's Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as cocoa, oleyl, tallow, or stearyl groups.

Other useful primary amines include primary ether amines, such as those represented by the formula, $R_{18}(OR_{19})_xNH_2$, wherein R_{18} is a divalent alkylene group having about 2 to about 6 carbon atoms; x is a number from one to about 150, or from about one to about five, or one; and R_{19} is a hydrocarbyl group from about 5 to about 150, or from 1 to about 24 carbon atoms. An example of an ether amine is available under the name SURFAM® amines produced and marketed by Mars Chemical Company, Atlanta, Georgia. Etheramines include those identified as SURFAM P14B (decyloxypropylamine), SURFAM P16A (linear C_{16}), and SURFAM P17B (tridecyloxypropylamine). The carbon chain lengths (i.e., C_{14} , etc.) of the SURFAMS described above and used hereinafter are approximate and include the oxygen ether linkage.

In another embodiment, the primary amine is a tertiary-aliphatic primary amine. Generally, the aliphatic group, and in one embodiment an alkyl group, contains from about 4 to about 30, or from about 6 to about 24, or from about 8 to about 22 carbon atoms. Usually the tertiary alkyl primary amines are monoamines represented by the formula $R_{20}-C(R_{21}')_2-NH_2$, wherein R_{20} is a hydrocarbyl group containing from 1 to about 28 carbon atoms and R_{21}' is a hydrocarbyl group containing from 1 to about 12 carbon atoms. Such amines are illustrated by tert-butylamine, tert-hexylamine, 1-methyl-1-aminocyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

Mixtures of amines are also useful for the purposes of this invention. Illustrative of amine mixtures of this type are "Primene 81R" which is a mixture of C_{11} - C_{14} tertiary alkyl primary amines and "Primene JMT" which is a similar mixture of C_{18} - C_{22} tertiary alkyl primary amines (both are available from Rohm and Haas Company). The tertiary alkyl primary amines and methods for their preparation are known to those of ordinary skill in the art. The tertiary alkyl primary amine useful for the purposes of this invention and methods for their preparation are described in U.S. Patent 2,945,749, which is hereby incorporated by reference for its teaching in this regard.

In another embodiment, the amine is a secondary amine. Specific examples of secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine, ethylamylamine and the like. In one embodiment, the secondary amines may be cyclic amines such as piperidine, piperazine, morpholine, etc.

In one embodiment, the dithiocarbamate compound (A) is prepared by reacting one or more dithiocarbamic acids or salts with one or more of the above unsaturated amides. If the reaction products of the dithiocarbamic acid or salt and an unsaturated amide has at least one additional NH group which are capable of reacting, then the reaction product may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. The reaction products of dithiocarbamic acids and salts with unsaturated amides are disclosed in U.S. Patents 4,758,362 (Butke) and 4,997,969 (Luciani), which patents are incorporated by reference for their disclosures of dithiocarbamic acids and salts, unsaturated amides and their reaction products including coupled products.

In one embodiment, the dithiocarbamate compound (A) is a reaction product of a dithiocarbamic acid or salt with one or more of the above described unsaturated acids, anhydrides or esters. If an unsaturated carboxylic acid or anhydride is used, an ester may then be formed by subsequent reaction of the dithiocarbamate-unsaturated carboxylic acid or anhydride adduct with an alcohol, such as those alcohols discussed above. In one embodiment, the dithiocarbamate acid or salt is formed from diethylamine or dibutylamine and carbon disulfide. The resulting dithiocarbamic acid is then reacted with methyl acrylate.

In one embodiment, the dithiocarbamate compound (A) is an alkylene-coupled dithiocarbamate. The dithiocarbamate may be represented by the Formula: $R_{22}(R_{23})N-C(S)-S-R_{24}-S-C(S)-N(R_{23})R_{22}$; wherein each R_{22} is independently a hydrogen; a hydrocarbyl group having from 1 to about 18 carbon atoms, or from 1 to about 10, or from 1 to about 6; or R_{22} taken together with R_{23} and a nitrogen atom form a five, six or seven member heterocyclic group; each R_{23} is independently a hydrocarbyl group having from 1 to about 18 carbon atoms, or R_{23} taken together with R_{22} and a nitrogen atom form a five, six or seven member heterocyclic group; and R_{24} is a hydrocarbylene group having from 1 to about 10, or from 1 to about 4 carbon atoms. In one embodiment, each R_{22} is independently a hydrogen or a propyl, butyl, amyl or hexyl group, or a butyl group. The above list encompasses all stereo arrangements of these groups, including isopropyl, n-propyl, isobutyl, sec-butyl, and n-butyl. When R_{23} is a hydrocarbyl group, it is defined the same as when R_{22} is a hydrocarbyl group. When R_{22} and R_{23} are taken together with a nitrogen atom to form a five, six or seven member heterocyclic group, the heterocyclic group is a pyrrolidinyl, a piperidinyl, a morpholinyl or a piperazinyl group. The heterocyclic group may contain one or more, or from one to three alkyl substituents on the heterocyclic ring. The alkyl substituents generally contain from about one to about six carbon atoms. Examples of heterocyclic groups include 2-methylmorpholinyl, 3-methyl-5-ethylpiperidinyl, 3-hexylmorpholinyl, tetramethylpyrrolidinyl, piperazinyl, 2,5-dipropylpiperazinyl, piperidinyl, 2-butylpiperazinyl, 3,4,5-triethylpiperidinyl, 3-hexylpyrrolidinyl, and 3-ethyl-5-isopropylmorpholinyl groups. In one embodiment, the heterocyclic group is a pyrrolidinyl or piperidinyl group.

Examples of R_{24} groups include an alkylene, arylene, alkarylene, and arylalkylene. In one embodiment, R_{22} is a methylene or ethylene group. In another embodiment, R_{24} is an arylene group, alkarylene group, or arylalkylene group having from 6 to about 10, or from 6 to about 8 carbon atoms. In one embodiment, R_{24} is a phenylmethylene, phenylethylene, phenyldiethylene, phenylene, or tolylene group.

U.S. Patent 3,876,550, issued to Holubec, describes lubricant compositions containing alkylene dithiocarbamic compounds. U.S. Patents 1,726,647 and 1,736,429, issued to Caldwell, describe phenylmethylene-bis(dithiocarbamates) and methods for making the same. These patents are incorporated by reference for their teachings relating to dithiocarbamate compounds and methods for preparing the same. A particularly useful dithiocarbamate is methylenebis(di-n-butyl dithiocarbamate).

In another embodiment, the dithiocarbamate compound is a bis(S-alkyldithiocarbamoyl) disulfide. These materials have previously been referred to as sulfur-coupled dithiocarbamates. The disulfides are prepared by (A) reacting a sulfur halide with about a stoichiometric equivalent of (i) at least one olefinic hydrocarbon, or (ii) an aldehyde or ketone, at a temperature and for a period of time sufficient to produce a di(halo hydrocarbyl)sulfur intermediate or a dialdehyde or diketone sulfur intermediate, and (B) reacting the intermediate with a salt of a dithiocarbamate in an amount sufficient generally to replace both halo groups with the dithiocarbamate groups or to react with both carbonyl groups of the dialdehyde or diketone. The sulfur halide utilized in the first step (A) may be sulfur monochloride (i.e., S_2Cl_2), sulfur dichloride, sulfur monobromide, sulfur dibromide, or mixtures of any of the above sulfur halides with elemental sulfur in varying amounts.

The sulfur halide utilized in the first step (A) may be sulfur monochloride (i.e., S_2Cl_2), sulfur dichloride, sulfur monobromide, sulfur dibromide, or mixtures of any of the above sulfur halides with elemental sulfur in varying amounts. Various olefins and olefin mixtures may be used as the starting material in step (A). The olefins are disclosed below. Specific examples of aldehydes that may be reacted with sulfur halides include, for example, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, 2-ethyl-hexanal, and cyclohexanecarboxaldehyde. Examples of ketones include dimethyl ketone, methyl ethyl ketone, diethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, etc.

The bis(S-alkyldithiocarbamoyl) disulfides also may be prepared by a process which comprises the steps of (A) reacting an olefinic hydrocarbon with a halogen to produce a halogen-containing intermediate, and (B) reacting said intermediate with an alkali metal sulfide and a salt of a dithiocarbamate in an amount sufficient to replace the halogen groups present partially with dithiocarbamate groups and/or partially with sulfide groups. The bis(S-alkyldithiocarbamoyl) disulfides are described in U.S. Patent 2,599,350, issued to Rudel et al. This patent is incorporated by reference for its disclosure of bis(S-alkyldithiocarbamoyl) disulfide and methods of making the same.

(B) Dispersant or Detergent

As described above, the lubricating compositions contain from about 0.01% to about 3% by weight of at least one dispersant or detergent. Generally, the dispersant or detergent is present in an amount from about 0.1% to about 3 %, preferably from about 0.2% to about 2%, more preferably from about 0.3% to about 1.5% by weight of the lubricating composition. The dispersants include acylated amines, carboxylic esters, Mannich reaction products, hydrocarbyl substituted amines, and mixtures thereof. In one embodiment, the dispersant or detergent is a boron containing dispersant or detergent.

The acylated amines include reaction products of one or more carboxylic acylating agent and one or more amine. The carboxylic acylating agents include fatty acids, isoaliphatic acids, dimer acids, addition dicarboxylic acids, trimer acids, addition tricarboxylic acids, and hydrocarbyl substituted carboxylic acylating agents. In one embodiment, the carboxylic acylating agent is a fatty acid. The fatty acids generally contain from about 8 to about 30, or from about 12 to about 24 carbon atoms. Examples of fatty acids include palmitoleic acid, oleic, linoleic, linolenic, erucic acid, lard oil acid, soybean oil acid, tall oil and rosin acid.

In another embodiment, the carboxylic acylating agents include isoaliphatic acids. Such acids contain a principal saturated, aliphatic chain typically having from about 14 to about 20 carbon atoms and at least one, but usually no more than about four, pendant acyclic lower alkyl groups. Specific examples of such isoaliphatic acids include 10-methyl-tetradecanoic acid, 3-ethyl-hexadecanoic acid, and 8-methyl-octadecanoic acid. The isoaliphatic acids include branched-chain acids prepared by oligomerization of commercial fatty acids, such as oleic, linoleic and tall oil fatty acids.

The dimer acids include products resulting from the dimerization of unsaturated fatty acids and generally contain an average from about 18 to about 44, or from about 28 to about 40 carbon atoms. Dimer acids are described in U.S. Patents 2,482,760, 2,482,761, 2,731,481, 2,793,219, 2,964,545, 2,978,468, 3,157,681, and 3,256,304, the entire disclosures of which are incorporated herein by reference.

In another embodiment, the carboxylic acylating agents are addition carboxylic acylating agents, which are addition (4+2 and 2+2) products of an unsaturated fatty acid, such as tall oil acids and oleic acids, with one or more unsaturated carboxylic reagents, which are described below. These acids are taught in U.S. Patent No. 2,444,328, the disclosure of which is incorporated herein by reference.

In another embodiment, the carboxylic acylating agent is a hydrocarbyl substituted carboxylic acylating agent. The hydrocarbyl substituted carboxylic acylating agents are prepared by a reaction of one or more olefins or polyalkenes with one or more unsaturated carboxylic reagent. The unsaturated carboxylic reagents include unsaturated carboxylic acids per se and functional derivatives thereof, such as anhydrides, esters, amides, imides, salts, acyl halides, and nitriles. The unsaturated carboxylic reagent include mono, di, tri or tetracarboxylic reagents. Specific examples of useful monobasic unsaturated carboxylic acids are acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, 2-phenylpropenoic acid, etc. Exemplary polybasic acids include maleic acid, maleic anhydride, fumaric acid, mesaconic acid, itaconic acid and citraconic acid. Generally, the unsaturated carboxylic reagent is maleic anhydride, acid or lower ester, e.g. those containing less than eight carbon atoms.

The hydrocarbyl group generally contains from about 8 to about 300, or from about 12 up to about 200, or from about 16 up to about 150, or from about 30 to about 100 carbon atoms. In one embodiment, the hydrocarbyl group contains from about 8 up to about 40, or from about 10 up to about 30, or from about 12 up to about 24 carbon atoms. The hydrocarbyl group may be derived from an olefin. The olefins typically contain from about 3 to about 40, or from about 4 to about 24 carbon atoms. These olefins are preferably alpha-olefins (sometimes referred to as mono-1-olefins or terminal olefins) or isomerized alpha-olefins. Examples of the alpha-olefins include 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tetracosene, etc. Commercially available alpha-olefin fractions that can be used include the C₁₅₋₁₈ alpha-olefins, C₁₂₋₁₈ alpha-olefins, C₁₄₋₁₈ alpha-olefins, C₁₄₋₁₈ alpha-olefins, C₁₆₋₁₈ alpha-olefins, C₁₈₋₂₀ alpha-olefins, C₁₈₋₂₄ alpha-olefins, C₂₂₋₂₈ alpha-olefins, etc.

In another embodiment, the hydrocarbyl group is derived from a polyalkene. The polyalkene includes homopolymers and interpolymers of polymerizable olefin monomers having from 2 up to about 16, or from 2 up to about 6, or from 2 to about 4 carbon atoms. The olefins may be monoolefins, such as ethylene, propylene, 1-butene, isobutene, and 1-octene, or polyolefinic monomers, including diolefinic monomers, such 1,3-butadiene and isoprene. In one embodiment, the interpolymer is a homopolymer. In one embodiment, the homopolymer is a polybutene, such as a polybutene in which about 50% of the polymer is derived from butylene. The polyalkenes are prepared by conventional procedures. In one embodiment, the polyalkene is characterized as containing from about 8 up to about 300, or from about 30 up to about 200, or from about 35 up to about 100 carbon

atoms. In one embodiment, the polyalkene is characterized by an \overline{M}_n (number average molecular weight) of at least about 400 or at least about 500. Generally, the polyalkene is characterized by having an \overline{M}_n from about 500 up to about 5000, or from about 700 up to about 3000, or from about 800 up to about 2500, or from about 900 up to about 2000. In another embodiment, \overline{M}_n varies from about 500 up to about 1500, or from about 700 up to about 1300, or from about 800 up to about 1200.

The abbreviation \overline{M}_n is the conventional symbol representing number average molecular weight. Gel permeation chromatography (GPC) is a method which provides both weight average and number average molecular weights as well as the entire molecular weight distribution of the polymers. For purpose of this invention a series of fractionated polymers of isobutene, polyisobutene, is used as the calibration standard in the GPC. The techniques for determining \overline{M}_n and \overline{M}_w values of polymers are well known and are described in numerous books and articles. For example, methods for the determination of \overline{M}_n and molecular weight distribution of polymers is described in W.W. Yan, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatographs", J. Wiley & Sons, Inc., 1979.

In another embodiment, the polyalkenes have a \overline{M}_n from about 1300 up to about 5000, or from about 1500 up to about 4500, or from about 1700 up to about 3000. The polyalkenes also generally have a $\overline{M}_w/\overline{M}_n$ from about 1.5 to about 4, or from about 1.8 to about 3.6, or from about 2.5 to about 3.2. The hydrocarbyl substituted carboxylic acylating agents are described in U.S. Patent 3,219,666 and 4,234,435, the disclosures of which is hereby incorporated by reference.

In another embodiment, the acylating agents may be prepared by reacting one or more of the above described polyalkenes with an excess of maleic anhydride to provide substituted succinic acylating agents wherein the number of succinic groups for each equivalent weight of substituent group, i.e., polyalkenyl group, is at least 1.3. The maximum number will generally not exceed 4.5. A suitable range is from about 1.3 to 3.5 and or from about 1.4 to about 2.5 succinic groups per equivalent weight of substituent groups.

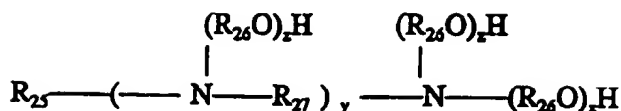
The carboxylic acylating agents are known in the art and have been described in detail, for example, in the following U.S. Patents 3,215,707 (Rense); 3,219,666 (Norman et al); 3,231,587 (Rense); 3,912,764 (Palmer); 4,110,349 (Cohen); and 4,234,435 (Meinhardt et al); and U.K. 1,440,219. The disclosures of these patents are hereby incorporated by reference. These patents are incorporated herein by reference for their disclosure of carboxylic acylating agents and methods for making the same.

The above-described carboxylic acylating agents are reacted with amines to form the acylated amines. The amines may be monoamines or polyamines. Useful amines include those amines disclosed in U.S. Patent 4,234,435 at Col. 21, line 4 to Col. 27, line 50, these passages being incorporated herein by reference. The amines may be any of the above described amines.

In one embodiment, the amine may be a hydroxyamine. Typically, the hydroxyamines are primary, secondary or tertiary alkanol amines or mixtures thereof. Such amines can be represented by the formulae: $H_2N-R'-OH$, $HR'_1-N-R'-OH$, and $(R'_1)_2-N-R'-OH$, wherein each R'_1 is independently a hydrocarbyl group having from one to about eight carbon atoms or hydroxyhydrocarbyl group having from one to about eight carbon atoms, or from one to about four, and R' is a divalent hydrocarbyl group of about two to about 18 carbon atoms, or from two to about four. The group $-R'-OH$ in such formulae represents the hydroxyhydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group. Where two R'_1 groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each R'_1 is independently a methyl, ethyl, propyl, butyl, pentyl or hexyl group. Examples of these alkanolamines include mono-, di-, and triethanolamine, diethylethanolamine, ethylethanolamine, butyldiethanolamine, etc.

The hydroxyamines may also be an ether N-(hydroxyhydrocarbyl)amine. These are hydroxypoly(hydrocarbyloxy) analogs of the above-described hydroxyamines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyhydrocarbyl) amines can be conveniently prepared by reaction of epoxides with aforescribed amines and may be represented by the formulae: $H_2N-(R'O)_x-H$, $HR'_1-N-(R'O)_x-H$, and $(R'_1)_2-N-(R'O)_x-H$, wherein x is a number from about 2 to about 15 and R_1 and R' are as described above. R'_1 may also be a hydroxypoly(hydrocarbyloxy) group.

In another embodiment, the amine is a hydroxyamine which may be represented by the formula



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wherein R_7 is a hydrocarbyl group containing from about 6 to about 30 carbon atoms; R_8 is an alkylene group having from about two to about twelve carbon atoms, preferably an ethylene or propylene group; R_9 is an alkylene group containing up to about 5 carbon atoms; y is zero or one; and each z is independently a number from zero to about 10, with the proviso that at least one z is zero.

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Useful hydroxyhydrocarbyl amines where y in the above formula is zero include 2-hydroxyethylhexylamine; 2-hydroxyethyloctylamine; 2-hydroxyethylpentadecylamine; 2-hydroxyethyloleamine; 2-hydroxyethylsoyamine; bis(2-hydroxyethyl)hexylamine; bis(2-hydroxyethyl)oleamine; and mixtures thereof. Also included are the comparable members wherein in the above formula at least one z is at least 2, as for example, 2-hydroxyethoxyethyl, hexylamine.

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In one embodiment, the amine may be a hydroxyhydrocarbyl amine, where referring to the above formula, y equals zero. These hydroxyhydrocarbyl amines are available from the Akzo Chemical Division of Akzona, Inc., Chicago, Illinois, under the general trade designations "Ethomeen" and "Propomeen". Specific examples of such products include: Ethomeen C/15 which is an ethylene oxide condensate of a coconut fatty acid containing about 5 moles of ethylene oxide; Ethomeen C/20 and C/25 which are ethylene oxide condensation products from coconut fatty acid containing about 10 and 15 moles of ethylene oxide, respectively; Ethomeen O/12 which is an ethylene oxide condensation product of oleyl amine containing about 2 moles of ethylene oxide per mole of amine; Ethomeen S/15 and S/20 which are ethylene oxide condensation products with stearyl amine containing about 5 and 10 moles of ethylene oxide per mole of amine, respectively; Ethomeen T/12, T/15 and T/25 which are ethylene oxide condensation products of tallow amine containing about 2, 5 and 15 moles of ethylene oxide per mole of amine, respectively; and Propomeen O/12 which is the condensation product of one mole of oleyl amine with 2 moles propylene oxide.

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The acylated amine may also be derived from a polyamine. The polyamines include alkoxyated diamines, fatty polyamine diamines, alkylenepolyamines, hydroxy containing polyamines, condensed polyamines, aryl-polyamines, and heterocyclic polyamines. Commercially available examples of alkoxyated diamines include those amines where y in the above formula is one. Examples of these amines include Ethoduomeen T/13 and T/20 which are ethylene oxide condensation products of N-tallowtrimethylenediamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.

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In another embodiment, the polyamine is a fatty diamine. The fatty diamines include mono- or dialkyl, symmetrical or asymmetrical ethylenediamines, propanediamines (1,2, or 1,3), and polyamine analogs of the above. Suitable commercial fatty polyamines are Duomeen C (N-coco-1,3-diaminopropane), Duomeen S (N-soya-1,3-diaminopropane), Duomeen T (N-tallow-1,3-diaminopropane), and Duomeen O (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available from Arma Chemical Co., Chicago, Illinois.

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In another embodiment, the amine is an alkylenepolyamine. Alkylenepolyamines are represented by the formula $HR_{28}N(Alkylene-N)_n-(R_{28})_2$, wherein each R_{28} is independently hydrogen; or an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms; n is a number from 1 to about 10, or from about 2 to about 7, or from about 2 to about 5; and the "Alkylene" group has from 1 to about 10 carbon atoms, or from about 2 to about 6, or from about 2 to about 4. In another embodiment, R_{28} is defined the same as R_1 above. Such alkylenepolyamines include methylenepolyamines, ethylenepolyamines, butylenepolyamines, propylenepolyamines, pentylenepolyamines, etc. The higher homologs and related heterocyclic amines, such as piperazines and N-amino alkyl-substituted piperazines, are also included. Specific examples of such polyamines are ethylenediamine, triethylenetetramine, tris-(2-aminoethyl)amine, propylenediamine, trimethylenediamine, tripropylenetetramine, triethylenetetraamine, tetraethylenepentamine, hexaethyleneheptamine, pentaethylenhexamine, etc. Higher homologs obtained by condensing two or more of the above-noted alkyleneamines are similarly useful as are mixtures of two or more of the aforescribed polyamines.

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In one embodiment, the polyamine is an ethylenepolyamine. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Ethylenepolyamines are often a complex mixture of poly-alkylenepolyamines including cyclic condensation products. Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave, as residue, what is often termed "polyamine bottoms". In general, alkylenepolyamine bottoms can be characterized as having less than 2%, usually less than 1% (by weight) material boiling below about 200°C. A typical sample of such ethylene-polyamine bottoms obtained from the Dow Chemical Company of Freeport, Texas designated "E-100" has a

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specific gravity at 15.6°C of 1.0168, a percent nitrogen by weight of 33.15 and a viscosity at 40°C of 121 centistokes. Gas chromatography analysis of such a sample contains about 0.93% "Light Ends" (most probably diethylenetriamine), 0.72% triethylenetetraamine, 21.74% tetraethylenepentaamine and 76.61% pentaethylenhexamine and higher analogs. These alkylene polyamine bottoms include cyclic condensation products such as piperazine and higher analogs of diethylenetriamine, triethylenetetraamine and the like. These alkylene polyamine bottoms may be reacted solely with the acylating agent or they may be used with other amines, polyamines, or mixtures thereof.

Another useful polyamine is a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. The hydroxy compounds are preferably polyhydric alcohols and amines. The polyhydric alcohols are described below. In one embodiment, the hydroxy compounds are polyhydric amines. Polyhydric amines include any of the above-described monoamines reacted with an alkylene oxide (e.g., ethylene oxide, propylene oxide, butylene oxide, etc.) having from two to about 20 carbon atoms, or from two to about four. Examples of polyhydric amines include tri-(hydroxypropyl)amine, tris-(hydroxymethyl)amino methane, 2-amino-2-methyl-1,3-propanediol, N,N,N',N'-tetraakis (2-hydroxypropyl) ethylenediamine, and N,N,N',N'-tetraakis (2-hydroxyethyl) ethylenediamine, preferably tris(hydroxymethyl) aminomethane (THAM).

Polyamines which may react with the polyhydric alcohol or amine to form the condensation products or condensed amines, are described above. Preferred polyamines include triethylenetetraamine (TETA), tetraethylenepentaamine (TEPA), pentaethylenhexamine (PEHA), and mixtures of polyamines such as the above-described "amine bottoms". The condensation reaction of the polyamine reactant with the hydroxy compound is conducted at an elevated temperature, usually from about 60°C to about 265°C, or from about 220°C to about 250°C in the presence of an acid catalyst.

The amine condensates and methods of making the same are described in PCT publication WO86/05501 and U.S. Patent 5,230,714 (Steckel) which are incorporated by reference for its disclosure to the condensates and methods of making. A particularly useful amine condensate is prepared from HPA Taft Amines (amine bottoms available commercially from Union Carbide Co. with typically 34.1 % by weight nitrogen and a nitrogen distribution of 12.3% by weight primary amine, 14.4% by weight secondary amine and 7.4% by weight tertiary amine), and tris(hydroxymethyl)aminomethane (THAM).

In another embodiment, the polyamines are polyoxyalkylene polyamines, e.g. polyoxyalkylene diamines and polyoxyalkylene triamines, having average molecular weights ranging from about 200 to about 4000, or from about 400 to about 2000. The preferred polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403, etc.". U.S. Patents 3,804,763 and 3,948,800 are expressly incorporated herein by reference for their disclosure of such polyoxyalkylene polyamines and acylated products made therefrom.

In another embodiment, the polyamines are hydroxy-containing polyamines. Hydroxy-containing polyamine analogs of hydroxy monoamines, particularly alkoxylated alkylene polyamines, e.g., N,N(diethanol)ethylene diamines can also be used. Such polyamines can be made by reacting the above-described alkylene amines with one or more of the above-described alkylene oxides. Similar alkylene oxide-alkanol amine reaction products may also be used such as the products made by reacting the above described primary, secondary or tertiary alkanol amines with ethylene, propylene or higher epoxides in a 1.1 to 1.2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art. Specific examples of hydroxy-containing polyamines include N-(2-hydroxyethyl)-ethylenediamine, N,N'-bis(2-hydroxyethyl)-ethylenediamine, 1-(2-hydroxyethyl)-piperazine, mono(hydroxypropyl)-substituted tetraethylenepentaamine, N-(3-hydroxybutyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above illustrated hydroxy-containing polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the above described polyamines are also useful.

In another embodiment, the polyamine is a heterocyclic polyamine. The heterocyclic polyamines include aziridines, azetidines, azolidines, tetra- and dihydropyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-diaminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl substituted piper-

idines, piperazine, aminoalkyl substituted piperazines, morpholine, aminoalkyl substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N'-diaminoethylpiperazine. Hydroxy heterocyclic polyamines are also useful. Examples include N-(2-hydroxyethyl)cyclohexylamine, 3-hydroxycyclopentylamine, parahydroxyaniline, N-hydroxyethylpiperazine, and the like.

Hydrazine and hydrocarbyl substituted-hydrazine may also be used to form the acylated nitrogen dispersants. At least one of the nitrogen atoms in the hydrazine must contain a hydrogen directly bonded thereto. Preferably there are at least two hydrogens bonded directly to hydrazine nitrogen and, more preferably, both hydrogens are on the same nitrogen. Specific examples of substituted hydrazines are methylhydrazine, N,N-dimethyl-hydrazine, N,N'-dimethylhydrazine, phenylhydrazine, N-phenyl-N'-ethylhydrazine, N-(para-tolyl)-N'-(n-butyl)-hydrazine, N-(paranitrophenyl)-hydrazine, N-(para-nitrophenyl)-N-methyl-hydrazine, N,N'-di(para-chlorophenyl)-hydrazine, N-phenyl-N'-cyclohexylhydrazine, and the like.

Acylated amines and methods for preparing the same are described in U.S. Patents 3,219,666; 4,234,435; 4,952,328; 4,938,881; 4,957,649; and 4,904,401. The disclosures of acylated nitrogen dispersants and other dispersants contained in those patents is hereby incorporated by reference.

In another embodiment, the dispersant may also be a carboxylic ester. The carboxylic ester is prepared by reacting at least one or more of the above carboxylic acylating agents, preferably a hydrocarbyl substituted carboxylic acylating agent, with at least one organic hydroxy compound and optionally an amine. In another embodiment, the carboxylic ester dispersant is prepared by reacting the acylating agent with at least one of the above-described hydroxyamines.

The organic hydroxy compound includes compounds of the general formula $R''(OH)_m$ wherein R'' is a monovalent or polyvalent organic group joined to the -OH groups through a carbon bond, and m is an integer from 1 to about 10 wherein the hydrocarbyl group contains at least about 8 aliphatic carbon atoms. The hydroxy compounds may be aliphatic compounds, such as monohydric and polyhydric alcohols, or aromatic compounds, such as phenols and naphthols. The aromatic hydroxy compounds from which the esters may be derived are illustrated by the following specific examples: phenol, beta-naphthol, alpha-naphthol, cresol, resorcinol, catechol, p,p'-dihydroxybiphenyl, 2-chlorophenol, 2,4-dibutylphenol, etc.

The alcohols from which the esters may be derived generally contain up to about 40 carbon atoms, or from 2 to about 30, or from 2 to about 10. They may be monohydric alcohols, such as methanol, ethanol, isooctanol, dodecanol, cyclohexanol, etc. The hydroxy compounds may also be polyhydric alcohols, such as alkylene polyols. In one embodiment, the polyhydric alcohols contain from 2 to about 40 carbon atoms, from 2 to about 20; and from 2 to about 10 hydroxyl groups, or from 2 to about 6. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butanediol, hexanediol; sorbitol; arabitol; mannitol; trimethylolpropane; sucrose; glucose; cyclohexanediol; erythritol; and pentaerythritols, including di- and tripentaerythritol.

The polyhydric alcohols may be esterified with monocarboxylic acids having from 2 to about 30 carbon atoms, or from about 8 to about 18, provided that at least one hydroxyl group remains unesterified. Examples of monocarboxylic acids include acetic, propionic, butyric and above described fatty acids. Specific examples of these esterified polyhydric alcohols include sorbitol oleate, including mono- and dioleate, sorbitol stearate, including mono- and distearate, glycerol oleate, including glycerol mono-, di- and trioate and erythritol octanoate.

The carboxylic ester dispersants may be prepared by any of several known methods. The method which is preferred because of convenience and the superior properties of the esters it produces, involves the reaction of the carboxylic acylating agents described above with one or more alcohol or phenol in ratios from about 0.5 equivalent to about 4 equivalents of hydroxy compound per equivalent of acylating agent. The esterification is usually carried out at temperatures above about 100°C, or between 150°C and 300°C. The water formed as a by-product is removed by distillation as the esterification proceeds. The preparation of useful carboxylic ester dispersant is described in U.S. Patents 3,522,179 and 4,234,435, and their disclosures are incorporated by reference.

The carboxylic ester dispersants may be further reacted with at least one of the above described amines and preferably at least one of the above described polyamines, such as a polyethylenepolyamine or a heterocyclic amine, such as aminopropylmorpholine. The amine is added in an amount sufficient to neutralize any nonesterified carboxyl groups. In one embodiment, the carboxylic ester dispersants are prepared by reacting from about 1 to about 2 equivalents, or from about 1.0 to 1.8 equivalents of hydroxy compounds, and up to about 0.3 equivalent, or from about 0.02 to about 0.25 equivalent of polyamine per equivalent of acylating agent. The carboxylic acid acylating agent may be reacted simultaneously with both the hydroxy compound and the amine. There is generally at least about 0.01 equivalent of the alcohol and at least 0.01 equivalent of the amine

although the total amount of equivalents of the combination should be at least about 0.5 equivalent per equivalent of acylating agent. These carboxylic ester dispersant compositions are known in the art, and the preparation of a number of these derivatives is described in, for example, U.S. Patents 3,957,854 and 4,234,435 which have been incorporated by reference previously.

5 In another embodiment, the dispersant may also be a hydrocarbyl-substituted amine. These hydrocarbyl-substituted amines are well known to those skilled in the art. These amines are disclosed in U.S. Patents 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,755,433; and 3,822,289. These patents are hereby incorporated by reference for their disclosure of hydrocarbyl amines and methods of making the same. Typically, hydrocarbyl substituted amines are prepared by reacting olefins and olefin polymers, including the above polyalkenes and halogenated derivatives thereof, with amines (mono- or polyamines). The amines may be any of the amines described above, preferably an alkylenepolyamine. Examples of hydrocarbyl substituted amines include poly(propylene)amine; N,N-dimethyl-N-poly(ethylene/propylene)amine, (50:50 mole ratio of monomers); polybutene amine; N,N-di(hydroxyethyl)-N-polybutene amine; N-(2-hydroxypropyl)-N-polybutene amine; N-polybutene-aniline; N-polybutenemorpholine; N-poly(butene)ethylenediamine; N-poly(propylene)trimethylenediamine; N-poly(butene)diethylenetriamine; N',N'-poly(butene)tetraethylenepentamine; N,N-dimethyl-N'-poly(propylene)-1,3-propylenediamine and the like.

In another embodiment, the dispersant may also be a Mannich dispersant. Mannich dispersants are generally formed by the reaction of at least one of the above described aldehydes, such as formaldehyde and paraformaldehyde, at least one of the above described amines and at least one alkyl substituted hydroxyaromatic compound. The reaction may occur from room temperature to about 225°C, or from about 50° to about 200°C, or from about 75°C to about 150°C. The amounts of the reagents is such that the molar ratio of hydroxyaromatic compound to formaldehyde to amine is in the range from about (1:1:1) to about (1:3:3).

The first reagent is an alkyl substituted hydroxyaromatic compound. This term includes the above described phenols, although the phenol need not be hindered. The hydroxyaromatic compounds are those substituted with at least one, and preferably not more than two, aliphatic or alicyclic groups having from about 6 up to about 400, or from about 30 up to about 300, or from about 50 up to about 200 carbon atoms. These groups may be derived from one or more of the above described olefins or polyalkenes. In one embodiment, the hydroxyaromatic compound is a phenol substituted with an aliphatic or alicyclic hydrocarbon-based group having an Mn of about 420 to about 10,000.

30 The third reagent is any amine described above. Preferably the amine is one or more of the above described polyamines, such as the polyalkylenepolyamines. Mannich dispersants are described in the following patents: U.S. Patent 3,980,569; U.S. Patent 3,877,899; and U.S. Patent 4,454,059 (herein incorporated by reference for their disclosure to Mannich dispersants).

In another embodiment, the dispersant is a borated dispersant. The borated dispersants are prepared by reacting one or more of the above dispersants with at least one boron compound. The boron compounds include boron oxide, boron oxide hydrate, boron trioxide, boron acids, such as boronic acid (i.e., alkyl-B(OH)₂ or aryl-B(OH)₂), including methyl boronic acid, phenyl-boronic acid, cyclohexyl boronic acid, p-heptylphenyl boronic acid and dodecyl boronic acid, boric acid (i.e., H₃BO₃), tetraboric acid (i.e., H₂B₄O₇), metaboric acid (i.e., HBO₂), boron anhydrides, boron amides and various esters of such boron acids.

40 In one embodiment, the boron compounds include mono-, di-, and tri-organic esters of boric acid and alcohols or phenols. Examples of the alcohols include methanol, ethanol, propanol, butanol, 1-octanol, benzyl alcohol, ethylene glycol, glycerol, and Cellosolve. Lower alcohols, having less than about 8 carbon atoms, and glycols, such as 1,2-glycols and 1,3-glycols, are especially useful. Methods for preparing the esters are known and disclosed in the art (such as "Chemical Reviews," pp. 959-1064, Vol. 56).

45 Typically, the borated dispersant contains from about 0.1% up to about 5%, or from about 0.5% up to about 4%, or from 0.7% up to about 3% by weight boron. In one embodiment, the borated dispersant is a borated acylated amine, such as a borated succinimide dispersant. Borated dispersants are described in 3,000,916; 3,087,936; 3,254,025; 3,282,955; 3,313,727; 3,491,025; 3,533,945; 3,666,662 and 4,925,983. These references are incorporated by reference for their disclosure of borated dispersants.

50 The following examples relate to dispersants useful in the present invention.

Example B-1

- 55 (a) An acylated nitrogen composition is prepared by reacting 3880 grams of the polyisobutenyl succinic anhydride, 376 grams of a mixture of triethylenetetramine and diethylene triamine (75:25 weight ratio), and 2785 grams of mineral oil in toluene at 150°C. The product is vacuum stripped to remove toluene.
- (b) A mixture of 62 grams (1 atomic proportion of boron) of boric acid and 1645 grams (2.35 atomic proportions of nitrogen) of the acylated nitrogen composition obtained from B-1(a) is heated at 150°C in ni-

trogen atmosphere for 6 hours. The mixture is then filtered and the filtrate is found to have a nitrogen content of 1.94% and a boron content of 0.33%.

Example B-2

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A mixture of 372 grams (6 atomic proportions of boron) of boric acid and 3111 grams (6 atomic proportions of nitrogen) of a acylated nitrogen composition, obtained by reacting 1 equivalent of a polybutenyl ($\overline{Mn}=850$) succinic anhydride, having an acid number of 113 (corresponding to an equivalent weight of 500), with 2 equivalents of a commercial ethylene amine mixture having an average composition corresponding to that of tetra-

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ethylene-pentamine, is heated at 150°C for 3 hours and then filtered. The filtrate is found to have a boron content of 1.64% and a nitrogen content of 2.56%.

Example B-3

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Boric acid (124 grams, 2 atomic proportions of boron) is added to the acylated nitrogen composition (556 grams, 1 atomic proportion of nitrogen) of Example B-2. The resulting mixture is heated at 150°C for 3.5 hours and filtered at that temperature. The filtrate is found to have a boron compound of 3.23% and a nitrogen content of 2.3%.

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Example B-4

(a) A reaction vessel is charged with 1000 parts of a polybutenyl ($\overline{Mn}=1000$ substituted succinic anhydride having a total acid number of 108 with a mixture of 275 grams of oil and 139 parts of a commercial mixture of polyamines corresponding to 85% E-100 amine bottoms and 15% diethylenetriamine. The reaction mixture is heated to 150 to 160°C and held for four hours. The reaction is blown with nitrogen to remove water.

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(b) A reaction vessel is charged with 1405 parts of the product of Example B-4(a), 229 parts of boric acid, and 398 parts of diluent oil. The mixture is heated to 100 to 150°C and the temperature maintained until water is removed. The final product contains 2.3% nitrogen, 1.9% boron, 33% 100 neutral mineral oil and a total base number of 60.

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In another embodiment, the dispersant or detergent (B) is an overbased metal salt and is present in an amount from about 0.5% to about 4%, or from about 0.7% to about 3%, or from about 0.9% to about 2% by weight of the lubricating composition. Overbased metal salts are characterized by having a metal content in excess of that which would be present according to the stoichiometry of the metal and the acidic organic compound. The amount of excess metal is commonly expressed in metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A salt having a metal ratio of 4.5 will have 3.5 equivalents of excess metal. The overbased salts generally have a metal ratio from about 1.5 up to about 40, or from about 2 up to about 30, or from about 3 up to about 25. In one embodiment, the metal ratio is greater than about 7, or greater than about 10, or greater than about 15.

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The overbased materials are prepared by reacting an acidic material, typically carbon dioxide, with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent for the acidic organic compound, a stoichiometric excess of a basic metal compound, and a promoter. Generally, the basic metal compounds are oxides, hydroxides, chlorides, carbonates, and phosphorus acids (phosphonic or phosphoric acid) salts, and sulfur acid (sulfuric or sulfonic) salts. The metals of the basic metal compounds are generally alkali, alkaline earth, and transition metals. Examples of the metals of the basic metal compound include sodium, potassium, lithium, magnesium, calcium, barium, titanium, manganese, cobalt, nickel, copper, zinc, and preferably sodium, potassium, calcium, and magnesium.

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The acidic organic compounds useful in making the overbased compositions of the present invention include carboxylic acylating agents, sulfonic acids, phosphorus containing acids, phenols, or mixtures of two or more thereof. Preferably, the acidic organic compounds are carboxylic acylating agents, or sulfonic acids. In one embodiment, the acidic organic compounds is one or more of the above described carboxylic acylating agent, such as a hydrocarbyl substituted carboxylic acylating agents, such as the hydrocarbyl substituted succinic anhydrides.

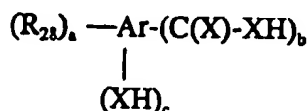
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In another embodiment, the carboxylic acylating agent is an alkylalkyleneglycol-acetic acid, or alkyl-polyethyleneglycol-acetic acid. Some specific examples of these compounds include: iso-stearyl-pentaerythritol-acetic acid; iso-stearyl-O-(CH₂CH₂O)₅CH₂CO₂Na; lauryl-O-(CH₂CH₂O)_{2.5}-CH₂CO₂H; lauryl-O-(CH₂CH₂O)_{3.3}CH₂CO₂H; oleyl-O-(CH₂CH₂O)₄-CH₂CO₂H; lauryl-O-(CH₂CH₂O)_{4.5}CH₂CO₂H; lauryl-O-(CH₂CH₂O)₁₀CH₂CO₂H; lauryl-O-(CH₂CH₂O)₁₆CH₂CO₂H; octyl-phenyl-O(CH₂CH₂O)₈CH₂CO₂H; octyl-phenyl-O-(CH₂CH₂O)₁₉CH₂CO₂H; 2-octyl-decanyl-O(CH₂CH₂O)₈CH₂CO₂H. These acids are available commercially.

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cially from Sandoz Chemical Co. under the tradename of Sandopan acids.

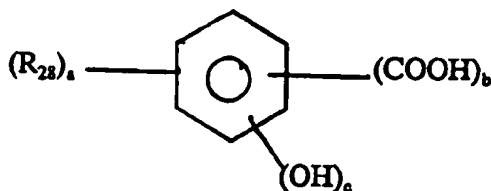
In another embodiment, the carboxylic acylating agents are aromatic carboxylic acids. A group of useful aromatic carboxylic acids are those of the formula



wherein R_{28} is an aliphatic hydrocarbyl group having from about 4 to about 400 carbon atoms, a is a number in the range of zero to about 4, Ar is an aromatic group, such as those discussed above, each X is independently sulfur or oxygen, preferably oxygen, b is a number in the range from one to about four, c is a number in the range of zero to about four, usually one or two, with the proviso that the sum of a , b and c does not exceed the number of valences of Ar . In one embodiment, R_{28} and a are such that there is an average of at least about eight aliphatic carbon atoms provided by the R_{28} groups.

The R_{28} group is a hydrocarbyl group that is directly bonded to the aromatic group Ar . R_{28} typically contains from about 6 to about 80, or from about 7 to about 30, or from about 8 to about 25, or from about 8 to about 15 carbon atoms. Examples of R_{28} groups include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, 5-chlorohexyl, 4-ethoxypentyl, 3-cyclohexyloctyl, 2,3,5-trimethylheptyl, propylene tetramer, triisobutenyl and substituents derived from one of the above described olefins or polyalkenes.

Within this group of aromatic acids, a useful class of carboxylic acids are those of the formula



wherein R_{28} is defined above, a is a number in the range of from zero to about 4, or from 1 to about 3; b is a number in the range of 1 to about 4, or from 1 to about 2, c is a number in the range of zero to about 4, or from 1 to about 2, and or 1; with the proviso that the sum of a , b and c does not exceed 6. In one embodiment, R_{28} and a are such that the acid molecules contain at least an average of about 12 aliphatic carbon atoms in the aliphatic hydrocarbon substituents per acid molecule. Typically, b and c are each one and the carboxylic acid is a salicylic acid.

In one embodiment, the salicylic acids are hydrocarbyl substituted salicylic acids, wherein each hydrocarbyl substituent contains an average of at least about 8 carbon atoms per substituent and 1 to 3 substituents per molecule. In one embodiment, the hydrocarbyl substituent is derived from one or more above-described polyalkenes.

The above aromatic carboxylic acids are well known or can be prepared according to procedures known in the art. Carboxylic acids of the type illustrated by these formulae and processes for preparing their neutral and basic metal salts are well known and disclosed, for example, in U.S. Patents 2,197,832; 2,197,835; 2,252,662; 2,252,664; 2,714,092; 3,410,798; and 3,595,791.

In another embodiment, the acidic organic compound is a sulfonic acid. The sulfonic acids include sulfonic and thiosulfonic acids, preferably sulfonic acids. The sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic compounds. The oil-soluble sulfonic acids may be represented for the most part by one of the following formulae: $R_{29}-\text{T}-(\text{SO}_3)_a\text{H}$ and $R_{30}-(\text{SO}_3)_b\text{H}$, wherein T is a cyclic nucleus such as benzene, naphthalene, anthracene, diphenylene oxide, diphenylene sulfide, and petroleum naphthenes; R_{29} is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, etc.; $(R_{29})+\text{T}$ contains a total of at least about 15 carbon atoms; and R_{30} is an aliphatic hydrocarbyl group containing at least about 15 carbon atoms. Examples of R_{30} are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R_{30} are groups derived from petrolatum, saturated and unsaturated paraffin wax, and one or more of the above-described polyalkenes. The groups T , R_{29} , and R_{30} in the above Formulae can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, disulfide, etc. In the above Formulae, a and b are at least 1.

A preferred group of sulfonic acids are mono-, di-, and tri-alkylated benzene and naphthalene sulfonic acids

including their hydrogenated forms. Illustrative of synthetically produced alkylated benzene and naphthalene sulfonic acids are those containing alkyl substituents having from about 8 to about 30 carbon atoms, or from about 12 to about 30 carbon atoms, and or to about 24 carbon atoms. Specific examples of sulfonic acids are mahogany sulfonic acids; bright stock sulfonic acids; sulfonic acids derived from lubricating oil fractions having a Saybolt viscosity from about 100 seconds at 100°F to about 200 seconds at 210°F; petrolatum sulfonic acids; mono- and polywax-substituted sulfonic acids; alkylbenzene sulfonic acids (where the alkyl group has at least 8 carbons), dilauryl-beta-naphthyl sulfonic acids, and alkaryl sulfonic acids, such as dodecylbenzene "bottoms" sulfonic acids.

Dodecylbenzene "bottoms" sulfonic acids are the material leftover after the removal of dodecylbenzene sulfonic acids that are used for household detergents. The "bottoms" may be straight-chain or branched chain alkylates with a straight-chain dialkylate preferred. The production of sulfonates from detergent manufactured by-products by reaction with, e.g., SO_3 , is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

In another embodiment, the acidic organic compound is a phosphorus containing acid. The phosphorus containing acids are one or more of the above described phosphorus containing acids. In one embodiment, the phosphorus - containing acid is the reaction product of one or more of the above polyalkenes and a phosphorus sulfide. Useful phosphorus sulfide sources include phosphorus pentasulfide, phosphorus sesquisulfide, phosphorus heptasulfide and the like. The reaction of the polyalkene and the phosphorus sulfide generally may occur by simply mixing the two at a temperature above 80°C, or from about 100°C to about 300°C. Generally, the products have a phosphorus content from about 0.05% to about 10%, or from about 0.1% to about 5%. The relative proportions of the phosphorizing agent to the olefin polymer is generally from 0.1 part to 50 parts of the phosphorizing agent per 100 parts of the olefin polymer. The phosphorus containing acids are described in U.S. Patent 3,232,883, issued to LeSuer. This reference is herein incorporated by reference for its disclosure to the phosphorus containing acids and methods for preparing the same.

In another embodiment, the acidic organic compound is a phenol. The phenols may be represented by the formula $(\text{R}_{28})_a\text{-Ar}(\text{OH})_b$, wherein R_{28} is defined above; Ar is an aromatic group as described above; a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar, which is defined above. In one embodiment, a and b are each independently numbers in the range from one to about four, or from one to about two. In one embodiment, R_{28} and a are such that there is an average of at least about eight aliphatic carbon atoms provided by the R_{28} groups for each phenol compound.

Promoters are often used in preparing the overbased metal salts. The promoters, that is, the materials which facilitate the incorporation of the excess metal into the overbased material, are also quite diverse and well known in the art. A particularly comprehensive discussion of suitable promoters is found in U.S. Patents 2,777,874, 2,695,910, 2,616,904, 3,384,586 and 3,492,231. These patents are incorporated by reference for their disclosure of promoters. In one embodiment, promoters include the alcoholic and phenolic promoters. The alcoholic promoters include the alkanols of one to about 12 carbon atoms, such as methanol, ethanol, amyl alcohol, octanol, isopropanol, and mixtures of these and the like. Phenolic promoters include a variety of hydroxy-substituted benzenes and naphthalenes. A particularly useful class of phenols are the alkylated phenols of the type listed in U.S. Patent 2,777,874, e.g., heptylphenols, octylphenols, and nonylphenols. Mixtures of various promoters are sometimes used.

Acidic materials, which are reacted with the mixture of acidic organic compound, promoter, metal compound and reactive medium, are also disclosed in the above cited patents, for example, U.S. Patent 2,616,904. Those disclosures are incorporated by reference for their disclosure of such acidic materials. Included within the known group of useful acidic materials are liquid acids, such as formic acid, acetic acid, nitric acid, boric acid, sulfuric acid, hydrochloric acid, hydrobromic acid, carbamic acid, substituted carbamic acids, etc. Acetic acid is a very useful acidic material although inorganic acidic compounds such as HCl, SO_2 , SO_3 , CO_2 , H_2S , N_2O_3 , etc., are ordinarily employed as the acidic materials. Particularly useful acidic materials are carbon dioxide and acetic acid.

The methods for preparing the overbased materials, as well as overbased materials, are known in the prior art and are disclosed, for example, in the following U.S. Patent Nos.: 2,616,904; 2,616,905; 2,616,906; 3,242,080; 3,250,710; 3,256,186; 3,274,135; 3,492,231; and 4,230,586. These patents disclose processes, materials, which can be overbased, suitable metal bases, promoters, and acidic materials, as well as a variety of specific overbased products useful in producing the overbased systems of this invention and are, accordingly, incorporated herein by reference for these disclosures.

The temperature at which the acidic material is contacted with the remainder of the reaction mass depends to a large measure upon the promoting agent used. With a phenolic promoter, the temperature usually ranges

from about 80°C to about 300°C, and preferably from about 100°C to about 200°C. When an alcohol or mercaptan is used as the promoting agent, the temperature usually will not exceed the reflux temperature of the reaction mixture and preferably will not exceed about 100°C.

In one embodiment, the overbased metal salts are borated overbased metal salts. The borated overbased metals salts are prepared by reacting one or more of the above overbased metals salts with one or more of the above described boron compounds. The borated overbased metal salts generally contains from about 0.1 % up to about 15%, or from about 0.5% up to about 10%, or from about 1% up to about 8% by weight of the boron. Borated overbased compositions, lubricating compositions containing the same and methods of preparing borated overbased compositions are found in U.S. Patent 4,744,920, issued to Fischer et al; U.S. Patent 4,792,410 issued to Schwind et al and PCT Publication WO88/03144. The disclosures relating to the above are hereby incorporated by reference.

The following examples relate to borated overbased metal salts and methods of making the same. Unless the context indicates otherwise, here as well as elsewhere in the specification and claims, parts and percentages are by weight, temperature is in degrees Celsius and pressure is atmospheric pressure.

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Example B-5

(a) A mixture of 853 grams of methyl alcohol, 410 grams of blend oil, 54 grams of sodium hydroxide, and a neutralizing amount of additional sodium hydroxide is prepared. The amount of the latter addition of sodium hydroxide is dependent upon the acid number of the subsequently added sulfonic acid. The temperature of the mixture is adjusted to 49°C. 1070 grams of a mixture of straight chain dialkyl benzene sulfonic acid ($\overline{M}_w=430$) and blend oil (42% by weight active content) are added while maintaining the temperature at 49-57°C. 145 grams of polyisobutenyl (number average $\overline{M}_n=950$)-substituted succinic anhydride are added. 838 grams of sodium hydroxide are added. The temperature is adjusted to 71°C. The reaction mixture is blown with 460 grams of carbon dioxide. The mixture is flash stripped to 149°C, and filtered to clarity to provide the desired product. The product is an overbased sodium sulfonate having a base number (bromophenol blue) of 440, a metal content of 19.45% by weight, a metal ratio of 20, a sulfate ash content of 58% by weight, and a sulfur content of 1.35% by weight.

(b) A mixture of 1000 grams of the product from Example B-5(a) above, 0.13 gram of an antifoaming agent (kerosene solution of Dow Corning 200 Fluid having a viscosity of 1000 cSt at 25°C), and 133 grams of blend oil is heated to 74-79°C with stirring. 486 grams of boric acid are added. The reaction mixture is heated to 121°C to liberate water of reaction and 40-50% by weight of the CO₂ contained in the product from Example 1(a). The reaction mixture is heated to 154-160°C and maintained at that temperature until the free and total water contents are reduced to 0.3% by weight or less and approximately 1-2% by weight, respectively. The reaction product is cooled to room temperature and filtered. The filtrate has 6.1% boron, 14.4% sodium, and 35% 100 neutral mineral oil.

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Example B-6

(a) A mixture of 1000 grams of a primarily branched chain monoalkyl benzene sulfonic acid ($\overline{M}_w=500$), 771 grams of o-xylene, and 75.2 grams of polyisobutenyl (number average $\overline{M}_n=950$) succinic anhydride is prepared and the temperature is adjusted to 46°C. 87.3 grams of magnesium oxide are added. 35.8 grams of acetic acid are added. 31.4 grams of methyl alcohol and 59 grams of water are added. The reaction mixture is blown with 77.3 grams of carbon dioxide at a temperature of 49-54°C. 87.3 grams of magnesium oxide, 31.4 grams of methyl alcohol and 59 grams of water are added, and the reaction mixture is blown with 77.3 grams of carbon dioxide at 49-54°C. The foregoing steps of magnesium oxide, methyl alcohol and water addition, followed by carbon dioxide blowing are repeated once. O-xylene, methyl alcohol and water are removed from the reaction mixture using atmospheric and vacuum flash stripping. The reaction mixture is cooled and filtered to clarity. The product is an overbased magnesium sulfonate having a base number (bromophenol blue) of 400, a metal content of 9.3% by weight, a metal ratio 14.7, a sulfate ash content of 46.0%, and a sulfur content of 1.6% by weight.

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(b) A mixture of 1000 grams of the product from Example B-6(a) and 181 grams of diluent oil is heated to 79°C. Boric acid (300 grams) is added and the reaction mixture is heated to 124°C over a period of 8 hours. The reaction mixture is maintained at 121-127°C for 2-3 hours. A nitrogen sparge is started and the reaction mixture is heated to 149°C to remove water until the water content is 3% by weight or less. The reaction mixture is filtered to provide the desired product. The product contains 7.63% magnesium and 4.35% boron.

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Example B-7

(a) A reaction vessel is charged with 281 parts (0.5 equivalent) of a polybutenyl-substituted succinic anhydride derived from a polybutene ($\bar{M}_n=1000$), 281 parts of xylene, 26 parts of tetrapropenyl substituted phenol and 250 parts of 100 neutral mineral oil. The mixture is heated to 80°C and 272 parts (3.4 equivalents) of an aqueous sodium hydroxide solution are added to the reaction mixture. The mixture is blown with nitrogen at 1 scfh (standard cu. ft/hr) and the reaction temperature is increased to 148°C. The reaction mixture is then blown with carbon dioxide at 1 scfh for one hour and 25 minutes while 150 parts of water is collected. The reaction mixture is cooled to 80°C where 272 parts (3.4 equivalents) of the above sodium hydroxide solution is added to the reaction mixture and the mixture is blown with nitrogen at 1 scfh. The reaction temperature is increased to 140°C where the reaction mixture is blown with carbon dioxide at 1 scfh for 1 hour and 25 minutes while 150 parts of water is collected. The reaction temperature is decreased to 100°C and 272 parts (3.4 equivalents) of the above sodium hydroxide solution is added while blowing the mixture with nitrogen at 1 scfh. The reaction temperature is increased to 148°C and the reaction mixture is blown with carbon dioxide at 1 scfh for 1 hour and 40 minutes while 160 parts of water is collected. The reaction mixture is cooled to 90°C and where 250 parts of 100 neutral mineral oil are added to the reaction mixture. The reaction mixture is vacuum stripped at 70°C and the residue is filtered through diatomaceous earth. The filtrate contains 50.0% sodium sulfate ash (theoretical 53.8%) by ASTM D-874, total base number of 408, a specific gravity of 1.18 and 37.1% oil.

(b) A reaction vessel is charged with 700 parts of the product of Example B-7(a). The reaction mixture is heated to 75°C where 340 parts (5.5 equivalents) of boric acid is added over 30 minutes. The reaction mixture is heated to 110°C over 45 minutes and the reaction temperature is maintained for 2 hours. A 100 neutral mineral oil (80 parts) is added to the reaction mixture. The reaction mixture is blown with nitrogen at 1 scfh at 160°C for 30 minutes while 95 parts of water is collected. Xylene (200 parts) is added to the reaction mixture and the reaction temperature is maintained at 130-140°C for 3 hours. The reaction mixture is vacuum stripped at 150°C and 20 millimeters of mercury. The residue is filtered through diatomaceous earth. The filtrate contains 5.84% boron (theoretical 6.43) and 33.1% oil. The residue has a total base number of 309.

As previously indicated, the combination of the antioxidant (A) and the dispersant or detergent (B) are useful as additives for lubricants in which they can function to control oxidation and subsequent viscosity increase. They may be employed in a variety of lubricants based on diverse oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. These lubricants include crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines, and the like. They can also be used in gas engines, stationary power engines and turbines and the like. Automatic or manual transmission fluids, transaxle lubricants, gear lubricants, including open and enclosed gear lubricants, tractor lubricants, metal-working lubricants, hydraulic fluids and other lubricating oil and grease compositions can also benefit from the incorporation therein of the compositions of the present invention. They may also be used as wire rope, walking cam, way, rock drill, chain and conveyor belt, worm gear, bearing, and rail and flange lubricants.

The combination of the antioxidant (A) and the dispersant or detergent (B) may be used in lubricants or in concentrates. The concentrate may contain the above combination alone or with other components used in preparing fully formulated lubricants. The concentrate also contains a substantially inert organic diluent, which includes kerosene, mineral distillates, or one or more of the oils of lubricating viscosity discussed below. In one embodiment, the concentrates contain from 0.01%, or from about 0.1%, or from about 1% up to about 70% or up to about 80%, even up to about 90% by weight of the combination.

The combination of the antioxidant (A) or the dispersant or detergent (B) may be present in a final product, blend, or concentrate in any amount effective to act as antioxidation agents in lubricating compositions. Generally, the antioxidant (A) is present in an amount of at least about 2% by weight. The total amount of antioxidant (A) is equal to the sum of the amounts of all antioxidants in the lubricant. In one embodiment, the antioxidant is present in an amount from about 2.5% to about 10%, or from about 3% to about 8% by weight of the lubricating composition. The dispersant or detergent (B) is generally present in an amount from about 0.01% to about 4%, or from about 0.1% to about 3%, or from about 0.5% to about 2.5% by weight of the lubricating composition.

The lubricating compositions and methods of this invention employ one or more of the above described oils of lubricating viscosity. Additionally the lubricants may contain (C) at least one additive selected from the group consisting of (i) at least one sulfur containing antiwear or extreme pressure agent, (ii) at least one phosphorus or boron antiwear or extreme pressure agent, and (iii) mixtures thereof, provided that when (A) is a dithiocarbamate, then (C) is different from (A).

(C)(i) Sulfur Compounds

The combination of an antioxidant (A) and a dispersant or detergent (B) may be used in lubricating compositions together with a sulfur compound (C)(i). The sulfur compounds include sulfurized organic compounds and dithiocarbamate containing compounds. In one embodiment, the sulfur compound is present in an amount from about 0.5% up to about 10%, or from about 1% up to about 8%, or from about 2% up to about 7% by weight of the lubricating composition. The sulfur compounds (C)(i) include mono- or polysulfide compositions, or mixtures thereof. The sulfur compounds are generally characterized as having sulfide linkages containing an average from 1 up to about 10, or from about 2 up to about 8, or from about 3 up to about 4 sulfur atoms. In one embodiment, the organic polysulfides may be a mixture of di-, tri- or tetrasulfide materials, preferably having a majority of trisulfide being preferred. Materials having at least 70% trisulfide are preferred, with materials containing greater than 80% trisulfide more preferred.

Materials which may be sulfurized to form (C)(i) include oils, unsaturated fatty acids, such as those described above, unsaturated fatty esters, olefins or poly-olefins, terpenes, or Diels-Alder adducts. Oils which may be sulfurized are natural or synthetic oils, including mineral oils, lard oil, carboxylic acid esters derived from aliphatic alcohols and fatty acids or aliphatic carboxylic acids (e.g., myristyl oleate and oleyl oleate) sperm whale oil and synthetic sperm whale oil substitutes and synthetic unsaturated esters or glycerides.

The unsaturated fatty esters include fatty oils, that is, naturally occurring or synthetic esters of glycerol and one or more of the above fatty acids. Examples of fatty esters include animal fats, such as Neat's-foot oil, lard oil, depot fat, beef tallow, vegetable oils including cottonseed oil, corn oil, safflower oil, sesame oil, soybean oil, and sunflower seed oil. The unsaturated fatty esters also may be prepared by esterifying alcohols and polyols with a fatty acid. The alcohols include the above described mono- and polyhydric alcohols, such as methanol, ethanol, propanol, butanol, ethylene glycol, neopentyl glycol, and glycerol.

The olefins, which may be sulfurized, contain at least one olefinic double bond, which is defined as a non-aromatic double bond. In its broadest sense, the olefin may be defined by the formula $R^{*1}R^{*2}C=CR^{*3}R^{*4}$, wherein each of R^{*1} , R^{*2} , R^{*3} , and R^{*4} is hydrogen, or an organic group. In general, the R^{*} groups in the above formula which are not hydrogen may be represented by $-(CH_2)_n-A$, wherein n is a number from 0 to about 10 and A is represented by $-C(R^{*5})_3$, $-COOR^{*5}$, $-CON(R^{*5})_2$, $-COON(R^{*5})_4$, $-COOM$, $-CN$, $-X$, $-YR^{*5}$ or $-Ar$, wherein: each R^{*5} is independently hydrogen, or a hydrocarbyl group, with the proviso that any two R^{*5} groups may be connected to form a ring of up to about 12 carbon atoms is formed; M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, barium, calcium); X is halogen (e.g., chloro, bromo, or iodo); Y is oxygen or divalent sulfur; Ar is an aromatic group of up to about 12 carbon atoms.

The olefinic compound is usually one in which each R group which is not hydrogen is independently alkyl, alkenyl or aryl group. In one embodiment, R^{*3} and R^{*4} are hydrogen and R^{*1} and R^{*2} are alkyl or aryl, especially alkyl having 1 up to about 30, or up to about 16, or up to about 8, or even up to about 4 carbon atoms. Olefins having from 2 up to about 30, or from about 3 up to about 16 (most often less than about 9) carbon atoms are particularly useful. Olefins having two to about 5 or to about 4 carbon atoms are particularly useful. Isobutene, propylene and their dimers, trimers and tetramers, and mixtures thereof are especially preferred olefins. Of these compounds, isobutylene and diisobutylene are particularly desirable. In one embodiment, the organic polysulfides may be a mixture of di-, tri- or tetrasulfide materials, preferably having a majority of trisulfide being preferred. Materials having at least 70% trisulfide are preferred, with materials containing greater than 80% trisulfide more preferred.

The sulfurized olefins may be produced by reacting sulfur monochloride with an olefin, and then treating the resulting product with an alkali metal sulfide in the presence of free sulfur. The resulting product is then treated with an inorganic base. The sulfurized olefin may also be prepared by the reacting, under superatmospheric pressure, the olefin with a mixture of sulfur and hydrogen sulfide in the presence, or absence, of a catalyst, followed by removal of low boiling materials. The olefins which may be sulfurized, the sulfurized olefin, and methods of preparing the same are described in U.S. Patents 4,119,549, 4,199,550, 4,191,659, and 4,344,854. The disclosure of these patents is hereby incorporated by reference for its description of the sulfurized olefins and preparation of the same.

In another embodiment, the organic polysulfide comprise sulfurized olefins prepared by the sulfochlorination of olefins containing four or more carbon atoms and further treatment with inorganic higher polysulfides according to U.S. Patent 2,708,199. The sulfurized olefins may be produced by (1) reacting sulfur monochloride with a stoichiometric excess of a lower olefin, e.g. containing two to about seven carbon atoms, (2) treating the resulting product with an alkali metal sulfide in the presence of free sulfur in a mole ratio of no less than 2:1 in an alcohol-water solvent, and (3) reacting that product with an inorganic base. This procedure is described in U.S. Patent 3,471,404, and the disclosure of U.S. Patent 3,471,404 is hereby incorporated by reference for its discussion of this procedure for preparing sulfurized olefins and the sulfurized olefins thus produced.

Generally, the olefin reactant contains from about 2 to 5 carbon atoms and examples include ethylene, propylene, butylene, isobutylene, amylene, etc.

The following example relates to an organic polysulfide.

5 Example S-1

Sulfur (526 parts, 16.4 moles) is charged to a jacketed, high-pressure reactor which is fitted with an agitator and internal cooling coils. Refrigerated brine is circulated through the coils to cool the reactor prior to the introduction of the gaseous reactants. After sealing the reactor, evacuating to about 2 torr and cooling, 920 parts
 10 (16.4 moles) of isobutene and 279 parts (8.2 moles) of hydrogen sulfide are charged to the reactor. The reactor is heated using steam in the external jacket, to a temperature of about 182°C over about 1.5 hours. A maximum pressure of 1350 psig is reached at about 168°C during this heat-up. Prior to reaching the peak reaction temperature, the pressure starts to decrease and continues to decrease steadily as the gaseous reactants are consumed. After about 10 hours at a reaction temperature of about 182°C, the pressure is 310-340 psig and
 15 the rate of pressure change is about 5-10 psig per hour. The unreacted hydrogen sulfide and isobutene are vented to a recovery system. After the pressure in the reactor has decreased to atmospheric, the sulfurized mixture is recovered as a liquid.

The mixture is blown with nitrogen at about 100°C to remove low boiling materials including unreacted isobutene, mercaptans and monosulfides. The residue after nitrogen blowing is agitated with 5% Super Filtrol and filtered, using a diatomaceous earth filter aid. The filtrate is the desired sulfurized composition which contains 42.5% sulfur.

In another embodiment, (C) is a sulfurized terpene compound. The term "terpene compound" as used in the specification and claims is intended to include the various isomeric terpene hydrocarbons having the empirical formula $C_{10}H_{16}$, such as contained in turpentine, pine oil and dipentenes, and the various synthetic and
 25 naturally occurring oxygen-containing derivatives. Pine-oil derivatives, which are commercially available from Hercules Incorporated, include alpha-terpineol (a high purity tertiary terpene alcohol); and Terpineol 318 Prime (a mixture containing about 60-65% weight alpha-terpineol and 15-20% weight beta-terpineol); Yarmor 302; Herco pine oil; Yarmor 302W; Yarmor F; and Yarmor 60.

In another embodiment, (C) is a sulfurized Diels Alder adduct. The sulfurized Diels Alder adduct is prepared
 30 by reacting a sulfur source, such as elemental sulfur, sulfur halides and organic polysulfides, including dialkyl polysulfides. A Diels-Alder reaction involves the reaction of at least one conjugated diene with at least one ethylenically or acetylenically unsaturated compound, these latter compounds being known as dienophiles. Piperylene, isoprene, methylisoprene, chloroprene, and 1,3-butadiene are among the preferred dienes for use in preparing the Diels-Alder adducts. Other dienes include linear 1,3-conjugated dienes, cyclic dienes, such
 35 as cyclopentadienes, fulvenes, 1,3-cyclohexadienes, 1,3,5-cycloheptatrienes, cyclooctatetraene, etc.

Dienophiles used in preparing the Diels-Alder adducts, include nitroalkenes; alpha, beta-ethylenically unsaturated carboxylic esters, acids or amides; ethylenically unsaturated aldehydes and vinyl ketones. The unsaturated carboxylic esters, acids and amides are described above. Specific examples of dienophiles include 1-nitrobutene-1, alkylacrylates, acrylamide, dibutylacrylamide, methacrylamide, crotonaldehyde; crotonic
 40 acid, dimethyldivinyl ketone, methylvinyl ketone, propionaldehyde, methylethynyl ketone, propiolic acid, propargylaldehyde, cyclopentenedione, 3-cyano-coumaran, etc. The sulfurized Diels-Alder adducts are readily prepared by heating a mixture of a sulfur source, preferably sulfur and at least one of the Diels-Alder adducts of the types discussed hereinabove at a temperature within the range of from about 110°C to just below the decomposition temperature of the Diels-Alder adducts. Temperatures within the range of about 110° to about
 45 200°C will normally be used. Generally, the molar ratio of sulfur source to Diels-Alder adduct is in a range of from about 0.75 up to about 4 or from about 1 up to about 3 or up to about 2.5. The Diels-Alder adducts are a well-known, art-recognized class of compounds prepared from dienes by Diels-Alder reaction. An example of a useful sulfurized Diels-Alder adduct is a sulfurized reaction product of butadiene and butyl-acrylate. Sulfurized Diels Alder adducts are described in U.S. Patents 3,498,915, 4,582,618, and Re 27331. These patents
 50 are hereby incorporated by reference for their disclosures of sulfurized Diels Alder adducts and methods of making the same.

In another embodiment, the sulfur compound (C)(i) is a dithiocarbamate containing compound. The dithiocarbamate-containing compounds include dithiocarbamate esters, dithiocarbamate amides, dithiocarbamic ethers, a sulfur coupled dithiocarbamates, and alkylene-coupled dithiocarbamates. These are described
 55 above. When the antioxidant (A) is a dithiocarbamate then (C) is different from (A).

(C)(ii) Phosphorus or Boron Agents

In one embodiment, the combination of the antioxidant (A) and the dispersant or detergent (B) are used in lubricating compositions in combination with at least one phosphorus or boron containing antiwear/extreme pressure agent (C)(ii). In this embodiment, (C)(ii) is present in an amount sufficient to impart antiwear, antiweld, and/or extreme pressure properties to the lubricants and functional fluids. The phosphorus or boron containing agents (C)(ii) are typically present in the lubricants and functional fluids at a level of up to about 20% by weight, preferably up to about 10% by weight, based on the total weight of the lubricant, functional fluid, or grease. Typically, the phosphorus or boron containing antiwear/extreme pressure agent is present in the lubricants and functional fluids at a level from about 0.01% up to about 10%, or from about 0.05% or up to about 4%, or from about 0.08% up to about 3% or from 0.1% to about 2% by weight.

Examples of phosphorus or boron containing antiwear/extreme pressure agents (C)(ii) include a phosphoric acid ester or salt thereof; a phosphite; a phosphorus-containing carboxylic ester, ether, or amide; a borated dispersant; an alkali metal or a mixed alkali metal, alkaline earth metal borate; a borated overbased metal salt; and a borate ester. The phosphorus acids include the phosphoric, phosphonic, phosphinic and thiophosphoric acids including dithiophosphoric acid as well as the monothiophosphoric acid, thiophosphinic and thiophosphonic acids. The phosphorus containing carboxylic esters, acids, ethers, or amides, the borated dispersants and the borated overbased metal salts have been described above. When the antioxidant (A) is a metal thiophosphate, then (C) is different than (A).

In one embodiment, (C)(ii) is a phosphorus acid ester is prepared by reacting one or more phosphorus acid or anhydride with an alcohol containing from 1 up to about 30, or from about 2 up to about 24, or from about 3 up to about 12 carbon atoms. The phosphorus acids or anhydrides and the alcohols are described above. Examples of useful phosphorus acid esters include the phosphoric acid di- and triesters prepared by reacting a phosphoric acid or anhydride with cresol alcohols. An example is tricresylphosphate.

In one embodiment, (C)(ii) may be a phosphorus ester prepared by reacting one or more dithiophosphoric acid with an epoxide or a glycol. This reaction product may be used alone, or further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide is generally an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, styrene oxide, etc. Propylene oxide is preferred. The glycols may be aliphatic glycols, having from 1 to about 12, or from about 2 to about 6, or about 2 or 3 carbon atoms, or aromatic glycols. Glycols include ethylene glycol, propylene glycol, catechol, resorcinol, and the like. The dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. patent 3,197,405 and U.S. patent 3,544,465 which are incorporated herein by reference for their disclosure to these.

The following Examples P-1 and P-2 exemplify the preparation of useful phosphorus acid esters.

Example P-1

Phosphorus pentoxide (64 grams) is added at 58°C over a period of 45 minutes to 514 grams of hydroxypropyl O,O-di(4-methyl-2pentyl)phosphorodithioate (prepared by reacting di(4-methyl-2pentyl)-phosphorodithioic acid with 1.3 moles of propylene oxide at 25°C). The mixture is heated at 75°C for 2.5 hours, mixed with a diatomaceous earth and filtered at 70°C. The filtrate contains 11.8% by weight phosphorus, 15.2% by weight sulfur, and an acid number of 87 (bromophenol blue).

Example P-2

A mixture of 667 grams of phosphorus pentoxide and the reaction product of 3514 grams of diisopropyl phosphorodithioic acid with 986 grams of propylene oxide at 50°C is heated at 85°C for 3 hours and filtered. The filtrate contains 15.3% by weight phosphorus, 19.6% by weight sulfur, and an acid number of 126 (bromophenol blue).

Acidic phosphoric acid esters may be reacted with an amine compound or metallic base to form an amine or metal salt. The salts may be formed separately and then the salt of the phosphorus acid ester may be added to the lubricating composition. Alternatively, the salts may also be formed in situ when the acidic phosphorus acid ester is blended with other components to form a fully formulated lubricating composition.

The amine salts of the phosphorus acid esters may be formed from ammonia or one or more of the above described amines, including monoamines and polyamines. In one embodiment, the amine is one or more of the above described tertiary aliphatic primary amines.

The metal salts of the phosphorus acid esters are prepared by the reaction of a metal base with the phosphorus acid ester. The metal base may be any metal compound capable of forming a metal salt. Examples of

metal bases include metal oxides, hydroxides, carbonates, sulfates, borates, or the like. The metals of the metal base include Group IA, IIA, IB through VIIB, and VIII metals (CAS version of the Periodic Table of the Elements). These metals include the alkali metals, alkaline earth metals and transition metals. In one embodiment, the metal is a Group IIA metal, such as calcium or magnesium, a Group IB metal, such as copper, a Group IIB metal, such as zinc, or a Group VIIB metal, such as manganese. Preferably the metal is magnesium, calcium, copper or zinc. Examples of metal compounds which may be reacted with the phosphorus acid include zinc hydroxide, zinc oxide, copper hydroxide, copper oxide, etc.

In one embodiment, (C)(ii) is a metal thiophosphate, preferably a metal dithiophosphate. The metal thiophosphate is prepared by means known to those in the art. Examples of metal dithiophosphates include zinc isopropyl, methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, barium di(nonyl) dithiophosphate, zinc di(cyclohexyl) dithiophosphate, copper di(isobutyl) dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, and zinc isopropyl secondary-butyl dithiophosphate.

The following Examples P-3 to P-6 exemplify the preparation of useful phosphorus acid ester salts.

Example P-3

A reaction vessel is charged with 217 grams of the filtrate from Example P-1. A commercial aliphatic primary amine (66 grams), having an average molecular weight of 191 in which the aliphatic radical is a mixture of tertiary alkyl radicals containing from 11 to 14 carbon atom, is added over a period of 20 minutes at 25-60°C. The resulting product has a phosphorus content of 10.2% by weight, a nitrogen content of 1.5% by weight, and an acid number of 26.3.

Example P-4

The filtrate of Example P-2 (1752 grams) is mixed at 25-82°C with 764 grams of the aliphatic primary amine used in of Example P-3. The resulting product has 9.95% phosphorus, 2.72% nitrogen, and 12.6% sulfur.

Example P-5

Phosphorus pentoxide (852 grams) is added to 2340 grams of iso-octyl alcohol over a period of 3 hours. The temperature increases from room temperature but is maintained below 65°C. After the addition is complete the reaction mixture is heated to 90°C and the temperature is maintained for 3 hours. Diatomaceous earth is added to the mixture, and the mixture is filtered. The filtrate has 12.4% phosphorus, a 192 acid neutralization number (bromophenol blue) and a 290 acid neutralization number (phenolphthalein).

The above filtrate is mixed with 200 grams of toluene, 130 grams of mineral oil, 1 gram of acetic acid, 10 grams of water and 45 grams of zinc oxide. The mixture is heated to 60-70°C under a pressure of 30 mm Hg. The resulting product mixture is filtered using a diatomaceous earth. The filtrate has 8.58% zinc and 7.03% phosphorus.

Example P-6

Phosphorus pentoxide (208 grams) is added to the product prepared by reacting 280 grams of propylene oxide with 1184 grams of O,O'-di-isobutylphosphorodithioic acid at 30-60°C. The addition is made at a temperature of 50-60°C and the resulting mixture is then heated to 80°C and held at that temperature for 2 hours. The commercial aliphatic primary amine identified in Example P-3 (384 grams) is added to the mixture, while the temperature is maintained in the range of 30-60°C. The reaction mixture is filtered through diatomaceous earth. The filtrate has 9.31% phosphorus, 11.37% sulfur, 2.50% nitrogen, and a base number of 6.9 (bromophenol blue indicator).

In another embodiment, (C)(ii) is a metal salt of (a) at least one dithiophosphoric acid and (b) at least one aliphatic or alicyclic carboxylic acid. The dithiophosphoric acids are described above. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3, or just one carboxylic acid group. The preferred carboxylic acids are those having the formula $R_{31}COOH$, wherein R_{31} is a hydrocarbyl group, preferably free from acetylenic unsaturation. Generally, R_{31} contains from about 2 up to about 40, or from about 3 up to about 24, or from about 4 up to about 12 carbon atoms. In one embodiment, R_{31} contains from about 4, or from about 6 up to about 12, or up to about 8 carbon atoms. In one embodiment, R_{31} is an alkyl group. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanoic, octodecanoic and eicosanoic acids, as well as olefinic acids such as oleic, linoleic, and linolenic acids, and linoleic dimer acid. A preferred carboxylic acid is 2-ethylhexanoic acid.

The metal salts may be prepared by merely blending a metal salt of a dithiophosphoric acid with a metal salt of a carboxylic acid in the desired ratio. The ratio of equivalents of dithiophosphoric acid to carboxylic acid is from about 0.5 up to about 400 to 1. The ratio may be from 0.5 up to about 200, or up to about 100, or up to about 50, or up to about 20 to 1. In one embodiment, the ratio is from 0.5 up to about 4.5 to 1, or from about 2.5 up to about 4.25 to 1. For this purpose, the equivalent weight of a dithiophosphoric acid is its molecular weight divided by the number of -PSSH groups therein, and the equivalent weight of a carboxylic acid is its molecular weight divided by the number of carboxy groups therein.

A second and preferred method for preparing the metal salts useful in this invention is to prepare a mixture of the acids in the desired ratio, such as those described above for the metal salts of the individual metal salts, and to react the acid mixture with one of the above described metal compounds. When this method of preparation is used, it is frequently possible to prepare a salt containing an excess of metal with respect to the number of equivalents of acid present; thus the metal salts may contain as many as 2 equivalents and especially up to about 1.5 equivalents of metal per equivalent of acid may be prepared. The equivalent of a metal for this purpose is its atomic weight divided by its valence. The temperature at which the metal salts are prepared is generally between about 30°C and about 150°C, preferably up to about 125°C. U.S. Patents 4,308,154 and 4,417,990 describe procedures for preparing these metal salts and disclose a number of examples of such metal salts. These patents are hereby incorporated by reference for those disclosures.

In another embodiment, (C)(ii) may be an aromatic phosphite as described above. In another embodiment, (C)(ii) may be an aliphatic phosphite. The phosphite may be a di- or trihydrocarbyl phosphite. Generally, each hydrocarbyl group has from 1 up to about 24, or from about 2 up to about 18, or from 3 up to about 8 carbon atoms. Examples of specific hydrocarbyl groups include propyl, butyl, hexyl, heptyl, octyl, oleyl, linoleyl, stearyl, and mixtures of two or more of thereof. In one embodiment, each hydrocarbyl group is independently propyl, butyl, pentyl, hexyl, heptyl, or oleyl. Phosphites and their preparation are known and many phosphites are available commercially. Particularly useful phosphites are dibutyl phosphite, and trioctyl phosphite.

In another embodiment, (C)(ii) is an alkali or an alkali metal and alkaline earth metal borate. These metal borates are generally a hydrated particulate metal borate which are known in the art. Alkali metal borates include mixed alkali and alkaline metal borates. These metal borates are available commercially. Representative patents disclosing suitable alkali and alkali metal and alkaline earth metal borates and their methods of manufacture include U.S. 3,997,454; 3,819,521; 3,853,772; 3,907,601; 3,997,454; and 4,089,790. These patents are incorporated by reference for their disclosures of the metal borates and methods of their manufacture.

In another embodiment, (C)(ii) is a borated fatty amine. The borated amines are prepared by reacting one or more of the above boron compounds with a fatty amine, e.g., an amine having from about four up to about eighteen carbon atoms. The borated fatty amines are prepared by reacting the amine with the boron compound at about 50°C to about 300°C, preferably about 100°C to about 250°C, and at a ratio of 3:1 to 1:3 equivalents of amine to equivalents of boron compound.

The borated fatty epoxides are generally the reaction product of one or more of the above boron compounds with at least one epoxide. The epoxide is generally an aliphatic epoxide having at least 8, preferably at least about 10, more preferably at least about 12 up to about 24, preferably up to about 20 carbon atoms. Examples of useful aliphatic epoxides include heptyl oxide, octyl oxide, stearyl oxide, oleyl oxide and the like. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having from about 14 to about 16 carbon atoms and from about 14 to about 18 carbon atoms. The borated fatty epoxides are generally known and are disclosed in U.S. Patent 4,584,115. This patent is incorporated by reference for its disclosure of borated fatty epoxides and methods for preparing the same.

In one embodiment, (C)(ii) is a borate ester. The borate esters may be prepared by reacting of one or more of the above boron compounds with one or more of the above identified alcohols. Typically, the alcohols contain from about 6 up to about 30, or from about 8 to about 24 carbon atoms. The methods of making such borate esters are known to those in the art.

In another embodiment, borate ester is a borated phospholipid. The borated phospholipids are prepared by reacting a combination of a phospholipid and a boron compound. Optionally, the combination may include an amine, an acylated nitrogen compound, a carboxylic ester, a Mannich reaction product, or a basic or neutral metal salt of an organic acid compound. These additional components are described above. Phospholipids, sometimes referred to as phosphatides and phospholipins, may be natural or synthetic. Naturally derived phospholipids include those derived from fish, fish oil, shellfish, bovine brain, chicken egg, sunflowers, soybean, corn, and cotton-seeds. Phospholipids may be derived from microorganisms, including blue-green algae, green algae, and bacteria.

The reactions usually occurs at a temperature from about 60°C up to about 200°C, or from about 90°C, or up to about 150°C. The reaction is typically accomplished in about 0.5 up to about 10 hours. The boron compound and phospho-lipid are reacted at an atomic proportion ratio of boron to phosphorus of 1-6:1 or 2-4:1,

or 3:1. When the combination includes additional components, the boron compound is reacted with the mixture of the phospholipid and one or more optional ingredients in an amount of one atomic proportion of boron to an equivalent of the mixture of a phospholipid and an optional ingredient in a ratio from about one, or about two up to about six, to about four to one. The equivalents of the mixture are based on the combined equivalents of phospholipid based on phosphorus and equivalents of the optional ingredients.

The antioxidant (A) and the dispersant or detergent (B) may be used in lubricating compositions together with other additives such as auxiliary extreme pressure agents, corrosion and oxidation inhibiting agents and metal deactivators. Auxiliary extreme pressure agents and corrosion- and oxidation-inhibiting agents which may be included in the lubricants of the invention are exemplified by chlorinated aliphatic hydrocarbons, such as chlorinated wax; phosphosulfurized hydrocarbons, such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium diheptylphenyl dithiocarbamate. The metal deactivators include dimercaptodithiadiazoles, such as the reaction products of octyl mercaptan and dimercaptodithiadiazole as well as the reaction product of heptylphenol, formaldehyde and dimercaptodithiadiazole. Many of the above-mentioned extreme pressure agents and corrosion- and oxidation-inhibitors also serve as antiwear agents.

Pour point depressants are an additive often included in the lubricating oils described herein. Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and polymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 which are hereby incorporated by reference for their relevant disclosures.

Antifoam agents are used to reduce or prevent the formation of stable foam. Typical antifoam agents include silicones or organic polymers. Additional antifoam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

The following examples relate to lubricating compositions of the present invention containing the antioxidant (A) and the dispersant or detergent (B).

Example L-1

A lubricant is prepared by incorporating 3.5% of dinonyldiphenylamine, 1.2% of the product of Example B-4, 0.1% oleylamide, 1.7% of the product of Example P-3, 4.6% of the product of Example S-1, 0.05% of a reaction product of C_9 mercaptan and dimercaptodithiadiazole, 0.1% of a reaction product of heptylphenol, formaldehyde and dimercaptodithiadiazole, 0.1% of a copolymer of methylacrylate and 2-ethylhexylacrylate, 30 ppm of Dow Corning 200 fluid, 0.04% by weight of monoisopropanolamine, and 2% by weight of a polybutene having a number average molecular weight of 2000, and 1.8% by weight of a 4 cSt PAO into a 75W-90 synthetic base fluid having a kinematic viscosity of 17.7 cSt.

Example L-2

A lubricant is prepared by incorporating 3.5% of dinonyldiphenylamine, 1.1% of the product of Example B-4, 0.03% of a substituted imidiazoline from oleylamine, 0.1% oleylamide, 1.7% of the product of Example P-3, 4.6% of the product of Example S-1, 0.05% of a reaction product of C_9 mercaptan and dimercaptodithiadiazole, 0.1% of a reaction product of heptylphenol, formaldehyde and dimercaptodithiadiazole, 0.03% of TOLAD 370 available from Petrolite Chemical, 0.1% of a copolymer of methylacrylate and 2-ethylhexylacrylate, 30 ppm of Dow Corning 200 fluid, and 1.7% by weight of a 4 cSt PAO into a 75w-90 synthetic base fluid.

Example L-3

A 75W-90 lubricant is prepared by incorporating 3.5% of dinonyldiphenylamine, 1.2% of the product of Example B-4, 0.03% of a substituted imidiazoline from oleylamine, 0.1% oleylamide, 1.7% of the product of Example P-3, 4.6% of the product of Example S-1, 0.1% of a reaction product of C_9 mercaptan and dimercaptodithiadiazole, 0.1% of a reaction product of heptylphenol, formaldehyde and dimercaptodithiadiazole, 0.03% of TOLAD 370 available from Petrolite Chemical, 0.1% of a copolymer of methylacrylate and 2-ethylhexylacrylate, 0.5% by weight of a maleic anhydride-styrene copolymer esterified with C_{8-18} and C_4 alcohols and post-treated with aminopropylmorpholine, 30 ppm of Dow Corning 200 fluid, 2.01% of diisodecylazelate, and 32% polybutene having a number average molecular weight of 2000 into 54.0% by weight of a 4 cSt PAO.

Example L-4

5 A 75W-90 lubricating composition is prepared by incorporating 3.5% of dinonyldiphenylamine, 1.4% of the product of Example B-6(b), 4.1% of the product of Example S-1, 1.6% of the product of Example P-3, 0.8% of a reaction product of dimercapthiadiazole and a carboxylic ester dispersant prepared by reacting a polybutenyl ($M_n=950$) substituted succinic anhydride with pentaerythritol and polyethylene polyamines, 0.3% triphenylphosphite, 0.3% glycerol monooleate, 0.1% by weight of a polymer of vinyl acetate, ethylacrylate and 2-ethylhexylacrylate, 1.9% of diisodecylazelate, 30 parts per million Dow Corning 200 fluid, 18% by weight a methacrylate polymer having a $M_n=14000$ and $M_w=25000$, 1% by weight of a methacrylate polymer having a $M_n=31000$ and $M_w=55000$ into 46.9% XHVI 100N isomerized wax basestock (0.01% sulfur/ 141 VI) and 20.1% by weight of a 6 cSt PAO.

Example L-5

15 A lubricating composition is prepared as described in Example L-1 except an SAE 10W30 base fluid is used in place of the SAE 75W-90 fluid.

Example L-6

20 A lubricant is prepared as described in Example L-3 except 3% of di-t-butylphenol is used in place of 3.5% of dinonyldiphenylamine.

Example L-7

25 A lubricant is prepared as described in Example L-4 except 1.6% of methylenebis(di-n-butyl dithiocarbamate) and 1.5% of 2,6-di-t-butyl-4-heptylphenol are used in place of dinonyldiphenylamine.

Example L-8

30 A lubricant is prepared as described in Example L-4 except 1.5% of the product of Example B-7(a) is used in place of the product of Example B-6(b).

Examples L-9 through L-14 are further examples of 75W-90 lubricating compositions using a 75W-90 synthetic base fluid into which is incorporated the additives described in the following table.

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|----|---|-----|------|------|------|------|------|
| 5 | | L-9 | L-10 | L-11 | L-12 | L-13 | L-14 |
| | Dinonyldiphenylamine | 1 | -- | -- | -- | 3.5 | 3.5 |
| | Triphenyl phosphite | 0.5 | -- | 0.2 | 0.3 | 0.7 | -- |
| 10 | Methylenebis(di-n-butyl-dithiocarbamate) | 1 | 3.0 | -- | -- | -- | -- |
| | Sulfur coupled tetrapropenyl phenol | -- | -- | 2.5 | -- | -- | -- |
| 15 | N-phenyl-1-naphthylamine | -- | -- | -- | 3.1 | -- | -- |
| | Product of Ex B-4 | 1.2 | -- | 1.1 | 1.1 | 0.9 | -- |
| | Product of Ex B-6(a) | -- | -- | -- | -- | -- | -- |
| 20 | Product of Ex B-6(b) | -- | 1.5 | -- | -- | -- | -- |
| | Product of Ex S-1 | -- | -- | 3.5 | 4.1 | 4.0 | 3.7 |
| | Product of Ex P-3 | -- | -- | -- | 1.3 | 0.8 | 1.2 |
| 25 | Reaction product of polybutenyl (Mn=850) succinic anhydride and tetraethylene pentamine | -- | -- | -- | -- | -- | 0.8 |
| 30 | | | | | | | |

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The lubricants containing the antioxidant and the dispersant or detergent show improved oxidation stability as measured by extended (e.g. 300 hours) L-60 Thermal Oxidation Stability Test. The method and apparatus are defined by CRC L-60 Thermal Stability test. Viscosity increase of the lubricants due to oxidation is minimized. Viscosity increase change is often below 100%. Further the viscosity increase is minimized while maintaining favorable carbon/varnish ratings.

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While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification.

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Claims

1. A lubricating composition comprising a major amount of an oil of lubricating viscosity with an iodine number less than about 9, (A) one or more antioxidants, wherein the total amount of antioxidant is at least about 2% by weight, (B) from about 0.01% to about 3% by weight of at least one dispersant or detergent, and optionally, (C) at least one additive selected from (i) a sulfur containing antiwear or extreme pressure agent, (ii) a phosphorus or boron antiwear or extreme pressure agent, and (iii) mixtures thereof, provided that (C) is different from (A).
2. The composition of claim 1 wherein the antioxidant (A) is selected from amine antioxidants, dithiophosphoric esters, phenol antioxidants, dithiocarbamates, aromatic phosphites, and sulfurized fatty oils and olefins.

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3. The composition of claim 1 wherein the antioxidant (A) is selected from aromatic substituted amines, hindered phenols, sulfur coupled phenols, aromatic phosphites, alkylene coupled dithiocarbamates and dithiocarbamate esters which are the reaction product of a dithiocarbamic acid or salt and one or more unsaturated amide, carboxylic acid, anhydride, or ester, and ether.
4. The composition of claim 1 wherein the antioxidant (A) is selected from a diphenylamine, an alkylene coupled dithiocarbamate and a dithiocarbamate ester prepared by reacting a dithiocarbamic acid or salt with an acrylate or methacrylate.
5. The composition of any preceding claim wherein (B) is at least one dispersant selected from an acylated amine, a carboxylic ester, a Mannich reaction product, and a hydrocarbyl substituted amine, or at least one detergent which is an overbased metal salt.
6. The composition of any one of claims 1-4 wherein (B) is at least one dispersant which is a reaction product of a hydrocarbyl substituted carboxylic acylating agent and a polyamine, or at least one detergent which is an overbased sodium, calcium, or magnesium carboxylate or sulfonate.
7. The composition of any one of claims 1-4 wherein (B) is selected from a borated acylated amine, a borated carboxylic ester, a borated Mannich reaction product, a borated hydrocarbyl substituted amine and a borated overbased metal salt.
8. The composition of any preceding claim wherein (C) is selected from an organic polysulfide; a metal thiophosphate; a phosphoric acid ester or salt thereof; a phosphite; a phosphorus-containing carboxylic acid, ester, ether, or amide; an alkali metal borate; a borated fatty amine; a borated phospholipid; and a borate ester.
9. The composition of any one of claims 1-7 wherein (C) is selected from an organic polysulfide; a phosphoric acid ester prepared by reacting a dithiophosphoric acid with an epoxide to form an intermediate, and the intermediate is further reacted with a phosphorus acid or anhydride, or a salt of the phosphoric acid ester; a phosphoric acid ester prepared by reacting a phosphorus acid or anhydride with at least one alcohol wherein each alcohol independently contains from about 1 to about 30 carbon atoms, or a salt of the phosphoric acid ester; and a dihydrocarbyl or trihydrocarbyl phosphite independently containing from one to about 30 carbon atoms in each hydrocarbyl group.
10. The composition of any preceding claim wherein the composition is a gear oil.
11. A method of lubricating a gear assembly comprising introducing the lubricating compositions of any one of claims 1-10 to a gear assembly and operating the assembly.